

Persistence of Pesticide Residues in Mineral and Organic Soils in the Fraser Valley of British Columbia

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In 1989, 12 vegetable farms in the Fraser Valley of British Columbia, Canada, were selected to determine the extent to which pesticide residues were accumulating in the soils. Organochlorine pesticides included BHC (71-899 ppb dry wt), heptachlor (16-614 ppb dry wt), aldrin and dieldrin (78-1280 ppb dry wt), chlordane (170-1800 ppb dry wt), and DDT (194-7162 ppb dry wt). They were found at the higher levels in organic muck soil, at the lower levels in silt loam soil, and were mostly nondetected in loamy sand. Endosulfan and its sulfate (13-14 901 ppb dry wt) were detected consistently in all three soils, and their concentrations were much higher in the muck soil than in the two mineral soils. Residues of organophosphorus and nitrogen-containing pesticides were not found consistently in all three soil types, and their concentrations were generally higher in muck than in mineral soils. Linuron (331-1260 ppb dry wt) was consistently detected in the muck soil and trifluralin (55-310 ppb dry wt) in the loamy sand.

INTRODUCTION

Almost two decades have passed since the use of organochlorine insecticides, including DDT, BHC, and cyclodienes, was phased out or banned in agriculture and forestry in Canada. The organochlorines are known to be highly persistent in soil. There has been considerable concern that some of these chemicals may contaminate water bodies remote from points of application as a result of leaching, surface runoff, and erosion. But since the mid 1970s, the use patterns of pesticides in agriculture have changed significantly. Organophosphorus, carbamate, and other nitrogen-containing pesticides became the primary chemicals used for control of insect pests and weeds. However, there is little information on whether these chemicals accumulate in soils and, if they do, to what extent. Insecticide residues in soils in southwestern Ontario were investigated in 1964 and 1965 (Harris et al., 1966), in 1964, 1966, and 1969 (Harris and Sans, 1971), and again in 1974 (Harris et al., 1977). According to the Ontario studies, DDT residues were present on all 15 farms tested; the concentrations of total DDT in soil were in the order of orchard farms > vegetable farms > tobacco farms > field crop farms. Levels of total DDT in 1974 were generally similar to or lower than those in 1964. Residue levels of cyclodienes in 1974 were about 50-75% of those in 1964. Organophosphorus insecticides had not accumulated significantly in mineral soils, but in organic soils there was a 10-fold increase in residues (Harris et al., 1977).

In 1989 we conducted an extensive study on 12 farms in the Fraser Valley of British Columbia (Figure 1) to determine the identities and concentrations of organochlorine, organophosphorus, and nitrogen-containing pesticides present in soils. The data generated will serve as a baseline for future studies. All 12 farms had been involved in vegetable farming for at least 25 years. They were selected as representing typical soils in the Fraser Valley. This paper reports our findings.

MATERIALS AND METHODS

Each of the 12 farms had a known history of at least 25 years in vegetable growing, including potatoes, cole crops, lettuce, and onions. The names of the growers participating are kept confidential, and the farms are identified by numbers only. Their

locations are shown in Figure 1 and the sizes and soil characteristics in Table I. On the basis of the organic matter content, farms 1-4 are classified as silt loam, farms 5-8 as muck, and farms 9-12 as loamy sand (Tables IV-VI).

Sampling of Soil. Prior to any further treatments with pesticide in 1989, soil samples were collected in mid-April from all 12 farms. To assure complete coverage, each farm was divided into subareas of about 1 ha for sampling. Twenty soil cores (20 cm × 2.5 cm diameter) were randomly taken from each subarea, and the soil cores taken from all subareas were pooled to obtain a representative sample for the farm. Immediately after collection, each pooled sample was thoroughly mixed in the laboratory by rolling, breaking the lumps, and rerolling up to five times. For convenience they were divided into smaller packages of about 1 kg and stored at -20 °C until used.

Extraction. Aliquots of 50 g of moist soil as collected from the field were mixed with 50 g of anhydrous Na₂SO₄ and extracted with 125 mL of ethyl acetate (pesticide grade) in 250-mL stoppered Erlenmeyer flasks by shaking for 0.5 h on a wrist-action shaker. The extracts were filtered through Whatman No. 1 filter paper into 500-mL round-bottom flasks. Extraction was repeated twice more in the same manner with 100 mL of ethyl acetate. The combined crude extracts were concentrated in a flash evaporator at 35 °C, and the final volumes were adjusted to 10 mL for cleanup.

Cleanup by Florisil Column Chromatography. Glass columns (30 cm × 1.1 cm i.d.) with Teflon stopcocks were packed from the bottom with a glass wool plug, 1.5 cm of Na₂SO₄, 6.0 cm of Florisil deactivated with 2% water, 1.5 cm of Na₂SO₄, and a glass wool plug. The packed columns were prewashed with 10 mL of ethyl acetate followed by 10 mL of hexane (pesticide grade). The crude extracts in ethyl acetate were diluted 1:10 with hexane. One-milliliter aliquots of the diluted crude extracts equivalent to 0.5 g of moist soil were quantitatively transferred to the cleanup columns, and the resulting eluates were collected. The columns were then eluted with 40 mL of 50% ethyl acetate in hexane. After addition of 1 mL of keeper (1% OV-101 in hexane), the combined eluates were concentrated to about 5 mL in a flash evaporator at 35 °C and then to 0.5 mL under a stream of nitrogen. The cleaned extracts were analyzed by GC-ECD (electron capture detector).

Cleanup by Activated Charcoal Column Chromatography. Glass columns (30 cm × 1.1 cm i.d.) with Teflon stopcocks were packed from the bottom with a glass wool plug, 1.5 cm of Na₂SO₄, 4 cm of a 2:5 (w/w) mixture of Nuchar C-Whatman CF-11 cellulose (Brown, 1975), 1.5 cm of Na₂SO₄, and a glass wool plug. The packed columns were prewashed with 10 mL of

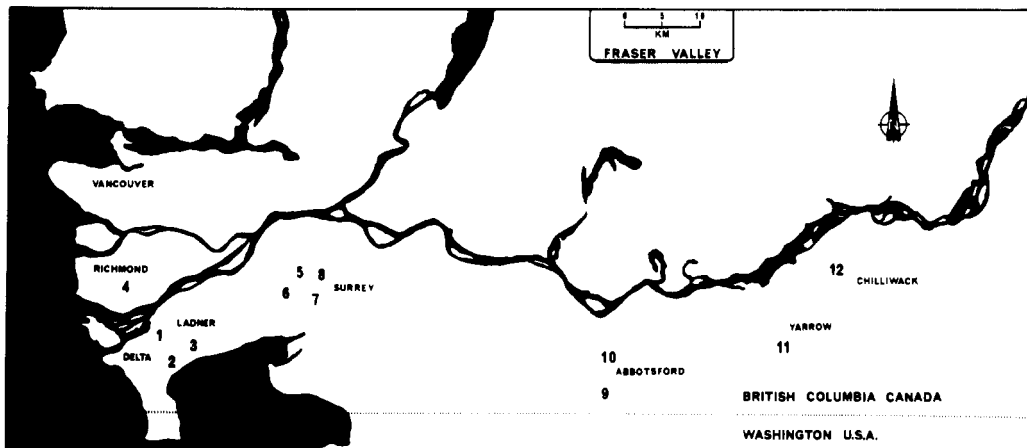


Figure 1. Location of 12 farms in the Fraser Valley that were selected for determination of pesticide residues in soil in 1989.

Table I. Characteristics of Soil on 12 Farms in the Fraser Valley of British Columbia

farm	location	size, ha	pH	moisture, %	composition, %				texture
					organic	sand	silt	clay	
1	Ladner	5	5.5	1.9	4.4	2.3	70.5	27.2	silt loam
2	Delta	9	5.8	2.0	4.4	6.8	66.2	27.0	silt loam
3	Ladner	8	5.6	1.8	3.7	1.3	71.4	27.3	silt loam
4	Richmond	4	5.4	2.3	6.5	5.7	70.6	23.7	silt loam
5	Surrey	6	4.8	5.0	27.0	3.4	66.4	30.2	silty clay loam
6	Surrey	6	5.2	5.6	31.4	3.7	67.5	28.8	silty clay loam
7	Surrey	4	5.1	8.8	56.3	12.7	54.8	32.5	silty clay loam
8	Surrey	6	5.5	9.0	49.5	28.5	53.3	18.2	silt loam
9	Abbotsford	6	6.1	0.7	1.8	79.8	16.4	3.8	loamy sand
10	Abbotsford	8	6.4	0.7	1.5	82.8	13.5	3.7	loamy sand
11	Yarrow	2	6.1	0.6	1.6	83.4	12.7	3.9	loamy sand
12	Chilliwack	6	6.1	0.8	1.0	83.1	13.3	3.6	loamy sand

methanol (HPLC grade) followed by 10 mL of ethyl acetate. Crude extracts equivalent to 10 g of moist mineral soil in 2 mL and 5 g of moist organic muck soil in 1 mL were quantitatively transferred to the cleanup columns, and the resulting eluates were collected. The columns were eluted with 40 mL of 40% methanol in ethyl acetate. After addition of 1 mL of keeper (1% OV-101 in hexane), the combined extracts were concentrated to about 5 mL in a flash evaporator at 35 °C and then to 0.5 mL under a stream of nitrogen. The cleaned extracts were analyzed by GC-NPD (nitrogen/phosphorus detector), GC-FPD (flame photometric detector), and GC-MSD (mass selective detector).

Cleanup by Gel Permeation Column Chromatography. A Pharmacia column, Model SR 25 (45 cm × 2.5 cm i.d.), was packed with Bio-Beads S-X12. The beads were swelled overnight in a 1:1 (v/v) mixture of dichloromethane and cyclohexane (both of pesticide grade) before the column was packed. An Eldex Model B-100-S high-pressure pump was used for solvent delivery, and a Valco Model C6PX sample injection valve equipped with a 5-mL injection loop was used to inject samples onto the column. Crude extracts equivalent to 10 g of moist mineral soil in 2 mL or 5 g of moist organic muck soil in 1 mL were adjusted to final volumes of 5 mL with a 1:1 (v/v) mixture of dichloromethane and cyclohexane for sample introduction onto the column. The column was eluted with the 1:1 (v/v) mixture of dichloromethane and cyclohexane. Fraction 1, consisting of the first 58 mL, was discarded, and fraction 2, consisting of the next 150 mL, was collected. After addition of 1 mL of keeper (1% OV-101 in hexane), fraction 2 containing the pesticides was concentrated to about 5 mL in a flash evaporator at 35 °C and then to 0.5 mL under a stream of nitrogen. The cleaned extracts were analyzed by GC-NPD, GC-FPD, and GC-MSD.

Oxidation Procedure. To determine quantitatively the pesticides that oxidized readily in soil, including disulfoton, phorate, oxydemeton-methyl, terbufos, demeton, and fensulfothion, aliquots of crude extracts equivalent to 10 g of mineral soil or 5 g of organic muck soil were purified by activated charcoal column chromatography. The cleaned extracts were oxidized with KMnO_4 (Szeto and Brown, 1982) to convert all parent compounds

and their oxidative metabolites to the corresponding sulfones for determination (Szeto and Brown, 1982; Szeto et al., 1986).

GC Analysis. Two gas chromatographs were used for pesticide determination: a Hewlett-Packard (H-P) Model 5880 gas chromatograph, equipped with a nitrogen/phosphorus detector (NPD) and a flame photometric detector (FPD), and an H-P Model 5890 gas chromatograph, equipped with an electron capture detector (ECD) and an H-P Model 5970 mass selective detector (MSD). For the NPD, an H-P cool on-column inlet and an H-P cross-linked methyl silicone capillary column (25 m × 0.31 mm i.d.; 0.33 μm thick) were used. For the other detectors, a split/splitless inlet at 220 °C and splitless mode and an H-P cross-linked methyl silicone capillary column (25 m × 0.20 mm i.d.; 0.33 μm thick) were used.

The detector temperatures were 385 °C for the ECD, 300 °C for the NPD, and 200 °C for the FPD. The makeup gas for the ECD was 5% methane in argon at 80 mL/min. The detector gas for the NPD consisted of 4 mL/min of hydrogen, 120 mL/min of air, and 30 mL/min of nitrogen. For the FPD, the detector gas consisted of 120 mL/min of hydrogen, 100 mL/min of air, and 30 mL/min of nitrogen. Helium at 105 kPa was the carrier gas for all capillary columns. Column temperature was programmed as follows for all columns: initial, 80 °C for 0.5 min; first program rate 25 °C/min to 185 °C; second program rate 5 °C/min to 225 °C and hold for 3 min, except for the screening of pesticides such as fenvalerate and cypermethrin (Table II), where the column temperature programmed to reach the temperature needed for elution was initial 90 °C for 1.0 min, first program rate 20 °C/min to 150 °C, second program rate 5 °C/min to 250 °C, and hold for 10 min.

All cleaned extracts were screened for organochlorine pesticides by ECD and for organophosphorus and nitrogen-containing pesticides by NPD. In screening, the pesticides were identified by their relative retention times. To supplement the screening by NPD, a highly selective FPD at phosphorus mode was used further to confirm the identity of organophosphorus pesticides. A list of all pesticides that can be identified by screening is given in Table II. After preliminary identifications of the pesticides

Table II. Pesticides That Can Be Detected by Screening with ECD and NPD, with Relative Retention Times

compd	detector	RRT ^a	compd	detector	RRT ^a
alachlor	NPD	0.91	diphenamide	NPD	1.03
aldrin	ECD	1.00	disulfoton oxon sulfone	NPD	1.01
allidochlor	NPD	0.41	disulfoton sulfone	NPD	1.16
ametryn	NPD	0.90	endosulfan I	ECD	1.18
aminocarb	NPD	0.75	endosulfan II	ECD	1.34
anilazine	NPD	1.08	endosulfan sulfate	ECD	1.51
azinphos-methyl	NPD	1.86	endrin	ECD	1.33
bendiocarb	NPD	0.66	EPTC	NPD	0.35
α -BHC	ECD	0.68	ethion	NPD	1.42
β -BHC	ECD	0.71	fensulfothion	NPD	1.36
bromacil	NPD	0.92	fensulfothion sulfone	NPD	1.41
captafol	ECD	1.56	fenvalerate	NPD	2.28
captan	NPD	1.05			2.33
carbaryl	NPD	0.88	folpet	NPD	1.10
carbofuran	NPD	0.71	fonofos	NPD	0.77
3-ketocarbofuran	NPD	0.79	fonofos oxon	NPD	0.69
3-hydroxycarbofuran	NPD	0.85	HCB	ECD	0.72
carbophenothion	NPD	1.45	heptachlor	ECD	0.91
chlorbromuron	NPD	1.09	heptachlor epoxide	ECD	1.08
γ -chlordane	ECD	1.14	iprodione	NPD	1.70
α -chlordane	ECD	1.19	lindane	ECD	0.74
chlordecone	ECD	1.51	linuron	NPD	0.96
chlorpropham	NPD	0.66	metalaxyl	NPD	0.91
chlorpyrifos	NPD	1.01	methidathion	NPD	1.14
chlorthal-dimethyl	ECD	1.01	methiocarb	NPD	0.94
cloethocarb	NPD	0.85	methoxychlor	ECD	1.81
cyanazine	NPD	0.96	mevinphos	NPD	0.39
cypermethrin	ECD	2.09	naled	NPD	0.59
		2.11	<i>trans</i> -nonachlor	ECD	1.22
		2.12	oxydemeton-methyl sulfone	NPD	0.88
		2.13	parathion	NPD	1.00
cyprazine	NPD	0.85	phorate oxon sulfone	NPD	0.85
<i>p,p'</i> -DDD	ECD	1.39	phorate sulfone	NPD	0.96
<i>o,p'</i> -DDE	ECD	1.15	phosmet	NPD	1.67
<i>p,p'</i> -DDE	ECD	1.25	pirimicarb	NPD	0.83
<i>o,p'</i> -DDT	ECD	1.42	desmethylpirimicarb	NPD	1.11
<i>p,p'</i> -DDT	ECD	1.58	prometryne	NPD	0.91
diazinon	NPD	0.79	propoxur	NPD	0.62
diazoxon	NPD	0.75	quintozone	ECD	0.76
dichlofenthion	ECD	0.86	simazine	NPD	0.67
dichlone	ECD	0.77	terbufos oxon sulfone	NPD	0.95
dichloran	ECD	0.69	terbufos sulfone	NPD	1.07
dieldrin	ECD	1.27	terbutryn	NPD	0.94
dinocap	ECD	1.59	tetradifon	ECD	1.88
		1.63	thionazin	NPD	0.54
		1.66	trichlorphon	NPD	0.42
		1.70	trifluralin	NPD	0.69
		1.76	vinclozolin	ECD	0.87

^aThe relative retention times are relative to aldrin for organochlorine pesticides and to parathion for organophosphorus and nitrogen-containing pesticides.

actually present in the soils (Table IV), each identity was confirmed by GC-MSD with full scan from 40 to 450 amu, except a few at levels below 10 ppb (dry wt) which were confirmed by selected ions.

On the basis of peak areas of the external standards injected before and after the sample, the residues were quantified with an ECD for organochlorine pesticides, a FPD for organophosphorus pesticides, and a NPD for nitrogen-containing pesticides. During analysis, the detector response was monitored with reference standards before and after sample injections. Results of quantification were accepted only when the detector response with reference standards fluctuated within $\pm 10\%$.

Evaluation of Analytical Methods. Control samples of soil (silt loam, pH 5.6, moisture 1.8%, organic matter content 3.7%, sand 1.3%, silt 71.4%, clay 27.3%) were collected from Ladner (Figure 1) and screened for pesticide residues according to the methods described using ECD and NPD. Ladner soil was chosen because of its high clay content and intermediate organic content. No gas chromatographic response that interfered with the analysis of pesticides listed in Table II was detected in any of these samples. Quadruplicate samples of 50 g of moist control soil were fortified at levels ranging from 0.25 to 1.0 ppm by adding 0.5 mL of an appropriate stock solution in acetone containing the pesticides positively identified in screening. After fortifi-

cation, they were equilibrated at room temperature in a fume hood for about 30 min before extraction. All fortified samples were extracted, purified, and analyzed as described.

RESULTS AND DISCUSSION

Recovery of Pesticides from Soil. Pesticides from fortified soil samples were recovered by the methods described. Not all of the pesticides which can be identified by either ECD or NPD, and confirmed by MSD, were evaluated. However, all pesticides that had been positively identified and confirmed were evaluated; their recoveries from fortified soil samples are given in Table III. The recoveries ranged from about 74% to 111% except allidochlor, of which only approximately 68% was recovered. The data generated from this study are reported here on a dry weight basis, without correction in accordance with recoveries. Based on the sensitivity of the NPD and the sample equivalence of cleaned extracts injected into the GC, the limits of detection on the dry weight basis were about 5 ppb in mineral soil and 10 ppb in organic muck soil for the organophosphorus and nitrogen-containing pesticides listed in Table II. The sensitivity of the ECD

Table III. Percentage Recoveries of Pesticides from Fortified Soil

compd	fortification, ppm	% recovery \pm SD (n = 4)
alachlor	0.50	78.7 \pm 2.6
	1.00	80.7 \pm 3.8
aldrin	0.50	74.5 \pm 2.8
allidochlor	0.25	68.7 \pm 2.2
α -BHC	0.50	77.6 \pm 4.7
β -BHC	0.50	91.0 \pm 6.4
bromacil	0.50	75.6 \pm 6.5
captafol	1.00	111.4 \pm 9.2
carbofuran	0.50	77.6 \pm 1.6
3-ketocarbofuran	0.50	77.3 \pm 2.1
α -chlordane	0.50	78.2 \pm 4.1
γ -chlordane	1.00	78.4 \pm 3.9
chlorpropham	0.50	82.3 \pm 2.0
chlorpyrifos	0.50	78.7 \pm 3.0
cloethocarb	0.50	80.8 \pm 2.5
<i>p,p'</i> -DDD	1.00	82.9 \pm 5.1
<i>p,p'</i> -DDE	1.00	80.9 \pm 4.4
<i>o,p</i> -DDT	1.00	81.2 \pm 4.9
<i>p,p'</i> -DDT	1.00	84.2 \pm 5.4
diazinon	0.50	74.0 \pm 4.4
dichloran	0.50	84.9 \pm 4.2
dieldrin	1.00	75.2 \pm 6.5
endosulfan I	1.00	81.8 \pm 5.6
endosulfan II	1.00	88.2 \pm 6.0
endosulfan sulfate	1.00	94.8 \pm 7.0
ethion	0.25	72.0 \pm 5.8
fensulfathion	0.50	74.6 \pm 2.1
fensulfathion sulfone	0.50	74.0 \pm 2.3
fonofos	0.25	78.6 \pm 2.6
HCB	0.50	72.6 \pm 2.2
heptachlor	0.50	79.7 \pm 5.4
heptachlor epoxide	0.50	82.2 \pm 5.8
iprodione	0.50	85.2 \pm 1.1
lindane	0.50	82.0 \pm 5.6
linuron	0.50	81.3 \pm 2.3
metalaxyl	0.50	78.5 \pm 4.9
<i>trans</i> -nonachlor	1.00	80.2 \pm 5.4
parathion	0.25	75.0 \pm 1.6
phorate	0.25	74.0 \pm 5.8
prometryne	0.50	108.7 \pm 6.7
quintozene	0.50	75.8 \pm 1.9
trifluralin	0.50	73.8 \pm 2.9
vinclozolin	0.50	101.8 \pm 5.3

was about 10 times higher than that of the NPD. However, the sample equivalence of cleaned extracts injected into the GC-ECD was about $1/10$ of that injected into the GC-NPD. Therefore, the limits of detection for the organochlorine pesticides listed in Table II were similar to those for organophosphorus and nitrogen-containing pesticides.

Residues of Organochlorine Pesticides in Soil. Residues and breakdown products of organochlorine pesticides including DDT, BHC, and cyclodienes were detected in the soils (Table IV). Depending on the organic matter content of the soil, concentrations of residues varied greatly between different soil types. They were highest in the muck with organic matter content ranging from 27% to 56% (farms 5–8), lower in the silt loam with organic matter content ranging from 3.7% to 6.5% (farms 1–4), and lowest in the loamy sand with organic matter content ranging from 1.0% to 1.8% (farms 9–12). Since the use of DDT and cyclodienes except endosulfan had been banned and the use of BHC and lindane had been phased out in the mid 1970s, our findings confirm the generally accepted theory that organic matter is the most important factor influencing the persistence of organochlorine pesticides in soil. Residues of organochlorine pesticides were shown to persist much longer in heavy soils with high organic matter content than in light soils with low organic matter content (Edwards, 1973). In the muck soil, heptachlor oxidized to its epoxide (Table IV). The mean

Table IV. Residues of Organochlorine Pesticides Detected in Soil on 12 Farms in the Fraser Valley, British Columbia, 1989

compd	mean residues, ppb dry wt (n/4) ^a range		
	loamy sand farms 9–12	silt loam farms 1–4	muck farms 5–8
α -BHC	ND ^b	ND	56 (3/4) 13–113
β -BHC	ND	ND	231 (3/4) 16–485
lindane	ND	ND	168 (3/4) 42–301
total BHC ^c	ND	ND	455 (3/4) 71–899
heptachlor	ND	ND	134 (3/4) 37–278
heptachlor epoxide	ND	16 (1/4)	174 (3/4) 85–336
total heptachlor ^d	ND	16 (1/4)	308 (3/4) 122–614
aldrin	ND	ND	78 (1/4) 692 (2/4)
dieldrin	ND	ND	104–1280 47–405
α -chlordane	ND	48 (1/4)	174 (3/4) 508 (3/4)
γ -chlordane	ND	63 (1/4)	201–1060 21–1060
<i>trans</i> -nonachlor	ND	59 (1/4)	148 (3/4) 36–335
total chlordane ^e	ND	170 (1/4)	830 (3/4) 284–1800
<i>p,p'</i> -DDE	10 (1/4)	61 (4/4) 31–135	296 (4/4) 188–363
<i>p,p'</i> -DDD	ND	ND	176 (4/4) 127–266
<i>p,p'</i> -DDT	ND	321 (4/4) 145–516	3525 (4/4) 2350–5610
<i>o,p</i> -DDT	ND	51 (4/4) 18–112	688 (4/4) 319–923
total DDT ^f	10 (1/4)	433 (4/4) 194–763	4685 (4/4) 2984–7162
endosulfan I	ND	ND	138 (4/4) 17–271
endosulfan II	42 (1/4)	45 (3/4) 18–59	1927 (4/4) 67–4790
endosulfan sulfate	38 (4/4) 13–68	251 (4/4) 38–372	3693 (4/4) 291–9840
total endosulfan ^g	80 (4/4) 13–110	296 (4/4) 56–431	5758 (4/4) 375–14901

^a Number of farms detected positive in a total of four farms of each soil type. ^b ND, nondetected; the limits of detection were 10 and 5 ppb (dry wt) in mineral soil and muck soil, respectively. ^c Total BHC = α -BHC + β -BHC + lindane. ^d Total heptachlor = heptachlor + heptachlor epoxide. ^e Total chlordane = α -chlordane + γ -chlordane + *trans*-nonachlor. ^f Total DDT = *p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT + *o,p*-DDT. ^g Total endosulfan = endosulfan I + endosulfan II + endosulfan sulfate.

concentrations of heptachlor (134 ppb) and its epoxide (174 ppb) were comparable, but the mean concentration of dieldrin (692 ppb) was much higher than that of aldrin (78 ppb). Although aldrin could oxidize to dieldrin in soil, the higher concentration of dieldrin in the muck soil was mainly due to its application as a soil insecticide. α - and γ -chlordane and *trans*-nonachlor are the major constituents of technical chlordane, which was used extensively as a soil insecticide in potatoes prior to the mid 1970s. Relatively high levels of total chlordane were still present in the muck soil in three of the four farms studied in 1989; the mean concentration was 830 ppb (Table IV).

The persistence of lindane, heptachlor, aldrin, and DDT and their metabolites in soils in the Fraser Valley was evaluated by comparing our findings of 1989 with the findings in 1971 reported by Oloffs et al. (1971). In that

Table V. Comparison of Residues of Organochlorine Pesticides in 2 Soils on 19 Farms in the Fraser Valley, British Columbia, 1971^a and 1989

compd	mean residues, ppb dry wt (n/total) ^b range			
	loamy sand		muck	
	1971	1989	1971	1989
lindane	95 (1/1)	ND ^c (0/4)	426 (8/10) 187-858	168 (3/4) 42-301
heptachlor	66 (1/1)	ND (0/4)	1381 (6/10) 274-4563	134 (3/4) 37-278
heptachlor epoxide	375 (1/1)	ND (0/4)	960 (6/10) 279-3563	174 (3/4) 85-336
total heptachlor ^d	441 (1/1)	ND (0/4)	2341 (6/10) 553-8126	308 (3/4) 122-614
aldrin	ND (0/1)	ND (0/4)	1187 (3/10) 200-2775	78 (1/4)
dieldrin	1165 (1/1)	ND (0/4)	2546 (6/10) 129-8563	689 (2/4) 104-1280
<i>p,p'</i> -DDE	343 (1/1)	11 (1/4)	540 (6/10) 234-778	296 (4/4) 188-363
<i>p,p'</i> -DDD	ND (0/1)	ND (0/4)	1139 (6/10) 515-1635	176 (4/4) 127-266
<i>p,p'</i> -DDT	4650 (1/1)	11 (1/4)	11606 (10/10) 3615-32250	3525 (4/4) 2350-5610
total DDT ^e	4993 (1/1)	22 (1/4)	13285 (10/10) 4364-34663	3997 (4/4) 2665-6239

^a Data adopted from Oloffs et al. (1971). ^b Number of farms detected positive in all farms studied in 1971 and in 1989. ^c ND, nondetected. The limits of detection were 10 and 5 ppb (dry wt) in mineral soil and muck soil, respectively, in the 1989 study but the limit of detection was not described in the 1971 study. ^d Total heptachlor = heptachlor + heptachlor epoxide. ^e Total DDT = *p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT.

study, residues of organochlorine pesticides were determined in 10 fields of muck soil in Surrey and in 1 field of loamy sand in Ladner. The farms in the present study are in the same areas with the same soil types. Data from both studies are given in Table V. Residues of organochlorine pesticides dissipated in both loamy sand and muck, much faster in the former than in the latter. In loamy sand, only *p,p'*-DDE and *p,p'*-DDT at low parts per billion levels were present in one of the four farms selected in 1989. In muck, residues of organochlorine pesticides were still present at high parts per billion levels in most farms selected for the 1989 study. The concentration detected by us in 1989 were about 10-40% of those reported by Oloffs et al. (1971) (Table V). DDT appeared to be more persistent than cyclodienes. The mean concentration of total DDT (*p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT) decreased by about 70% from 1971 (13 285 ppb) to 1989 (3997 ppb) (Table V). By comparison, the mean concentrations of cyclodienes including total heptachlor (heptachlor + heptachlor epoxide), aldrin, and dieldrin decreased by about 80-90% between 1971 and 1989 (Table V). Similar trends were reported by Harris et al. (1977) in their study on insecticide residues in soils in 1964 and 1974 on 15 farms in southwestern Ontario. Lindane appeared to dissipate at a slower rate in the muck than DDT and cyclodienes. The mean concentration decreased by about 60% from 1971 (426 ppb) to 1989 (168 ppb). However, our data also showed that the mean concentration of lindane was considerably lower than the mean concentrations of total heptachlor, aldrin plus its epoxide, dieldrin, and total DDT (Table V), indicating that lindane was in fact chemically less persistent than DDT and cyclodienes. Furthermore, the use of lindane was phased out, rather than completely banned, in the mid 1970s.

Some of the lindane residues detected in 1989 may have resulted from its limited use as a soil insecticide after the mid 1970s.

The dissipation of organochlorine pesticide residues from the loamy sand was almost complete, which may be attributed to the low content of organic matter in the soil (Edwards, 1973). The major contributing factor for the disappearance of organochlorine pesticide residues from mineral soil with low organic matter content is probably the rapid initial loss through volatilization. However, other factors such as leaching and erosion may play an important role also. Considering the high permeability of the Abbotsford Outwash aquifer in the general area of Abbotsford, Yarrow, and Chilliwack, it is likely that the groundwater may have been contaminated with organochlorine pesticides. In fact, detectable levels of some organonitrogen and organophosphorus pesticides were found in the groundwater in the reconnaissance study conducted by the National Hydrology Research Institute of Environment Canada in the Abbotsford Outwash aquifer (McNaughton et al., 1989). More research would be necessary to confirm whether groundwater contamination indeed occurs in this region.

Recently, some vegetable growers in the Fraser Valley have expressed an interest in organic farming. It is of considerable concern whether residues of organochlorine pesticides would accumulate in root crops grown in contaminated soils in the Fraser Valley. In loamy sand (farms 9-12) the silt loam (farms 1-4), the root crops would almost certainly be free of residues because the levels of organochlorine pesticide residues are so low. But root crops grown in the muck soils might well contain residues. However, it is well established that residues of organochlorine pesticides are tightly bound in muck soils because of their high organic content, which greatly reduces their possible uptake by the plants (Lichtenstein, 1959; Harris and Sans, 1967; Oloffs et al., 1971). In fact, Oloffs et al. (1971) reported that carrots grown in sand picked up residues of total DDT, aldrin, dieldrin, heptachlor, heptachlor epoxide, and lindane more readily than did those grown in contaminated muck soils. Using *p,p'*-DDT as an indicator, carrots grown in muck soils with about 10 ppm of *p,p'*-DDT contained about 0.027 ppm of residues. On the basis of the data of this study and of Oloffs et al. (1971), it is reasonable to conclude that root crops grown in the muck soils in the Fraser Valley might contain residues of organochlorine pesticides which had been phased out or completely banned in the mid 1970s. The residues would be negligible, however.

Endosulfan is the only cyclodiene still registered in Canada for control of insect pests in various food crops. Compared with other insecticides, the use of endosulfan is quite extensive in vegetables because it has wide-spectrum efficacy and is relatively inexpensive. Endosulfan is also much less persistent than the other organochlorines, including DDT, BHC, and other cyclodienes. Our data showed clearly that endosulfan did not persist in loamy sand and silt loam (Table IV). On one farm, in loamy sand, endosulfan was present at low levels, i.e., 80 ppb total (endosulfan I + endosulfan II + endosulfan sulfate). The frequency of occurrence and residue levels of endosulfan in silt loam were considerably higher. Endosulfan residues were present in three of the four farms studied, and the mean concentration of total endosulfan was 296 ppb. In muck soil, endosulfan persisted at high levels. Residues of endosulfan were present in all four farms, and the mean concentration of total endosulfan was 5758 ppb (Table IV). Endosulfan is highly toxic to

Table VI. Residues of Organophosphorus and Nitrogen-Containing Pesticides Detected in Soil on 12 Farms in the Fraser Valley, British Columbia, 1989

compd	mean residues, ppb dry wt (n/4) ^a		
	loamy sand farms 9-12	silt loam farms 1-4	muck farms 5-8
carbofuran	ND ^b	78 (1/4)	ND
chlorpyrifos	18 (2/4) 5-32	ND	296 (1/4)
diazinon	ND	18 (1/4)	ND
ethion	ND	ND	135 (2/4) 14-256
fensulfothion	ND	92 (1/4)	ND
fonofos	ND	ND	610 (2/4) 20-1200
parathion	ND	ND	111 (1/4)
phorate	ND	8 (1/4)	54 (1/4)
allidochlor	ND	ND	1360 (1/4)
chlorpropham	ND	ND	5520 (1/4)
linuron	ND	ND	657 (3/4) 331-1260
prometryne	ND	ND	429 (2/4) 219-639
trifluralin	164 (4/4) 55-310	236 (1/4)	ND
iprodione	ND	ND	1210 (1/4)

^a Number of farms detected positive in a total of four farms of each soil type. ^b ND, nondetected; the limits of detection were 10 and 5 ppb (dry wt) in mineral soil and muck soil, respectively.

fish (Spencer, 1982). The dissipation of endosulfan via surface runoff, especially from mineral soils, could contaminate the fish habitat for Pacific salmonids in the Fraser Valley. Wan (1989) studied the levels of selected pesticides, including endosulfan, in farm ditches leading to rivers in the Fraser Valley. Endosulfan was not found in ditch water, except on one farm shortly after a spray application. However, residues of endosulfan ranging from 2 to 150 ppb were consistently detected in the sediments. In view of its high fish toxicity and the relatively high levels encountered in the soils, especially in muck, it will be necessary to monitor periodically in the near future.

Residues of Organophosphorus and Nitrogen-Containing Pesticides in Soil. Residues of organophosphorus and nitrogen-containing pesticides were detected in all three soils (Table VI). In general, concentrations were higher in muck than in mineral soils. The findings again confirm the general theory that pesticides are more persistent in organic than in mineral soil. Unlike the residues of organochlorines which were found consistently on the 12 farms (Table IV), no organophosphorus and nitrogen-containing pesticide was consistently detected. Our findings suggest that these pesticides were nonpersistent. Whatever residues were detected on a farm were probably derived from the pesticides applied in the previous growing season. Allidochlor (1360 ppb), chlorpropham (5520 ppb), and iprodione (1210 ppb) were found in the muck soil from a single farm but not in any other. Trifluralin, a pre-emergence herbicide, is not recommended in the production guide for use on soils with organic matter content greater than 12%. Our results confirmed this use pattern in the Fraser Valley resulting from the farmers' adherence to recommendations: trifluralin was consistently found in the mineral soils but not in the muck soils, whose organic matter content is well above 12% (Table VI). Similarly, linuron is not recommended for use on mineral soils with low organic matter content. Our results again confirmed this use pattern: linuron was consistently found only in muck soils. The mean concentrations of trifluralin and linuron were 164

ppb in the loamy sand and 657 ppb in the muck, respectively (Table VI). On the basis of 10 years of studies on insecticide residues in soils on 15 farms in southwestern Ontario, Harris et al. (1977) concluded that no significant accumulation of organophosphorus insecticides was apparent in mineral soils but that these residue levels increased 10-fold in soils high in organic matter from 1964 to 1974. Since there are no previous data on the residue levels of organophosphorus and nitrogen-containing pesticides in soils in the Fraser Valley, it is difficult to conclude whether residues of these pesticides have accumulated significantly. Therefore, these 1989 data will serve as a baseline for future studies on accumulation of chemicals in soils in the region.

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Registry No. α -BHC, 319-84-6; β -BHC, 319-85-7; *p-p'*-DDE, 72-55-9; *p,p'*-DDD, 72-54-8; *p,p'*-DDT, 50-29-3; *o,p'*-DDT, 789-02-6; total BHC, 135367-00-9; lindane, 58-89-9; heptachlor, 76-44-8; heptachlor epoxide, 1024-57-3; aldrin, 309-00-2; dieldrin, 60-57-1; α -chlordane, 5103-71-9; γ -chlordane, 5566-34-7; *trans*-nonachlor, 39765-80-5; endosulfan I, 959-98-8; endosulfan II, 33213-65-9; endosulfan sulfate, 1031-07-8; carbofuran, 1563-66-2; chlorpyrifos, 2921-88-2; diazinon, 333-41-5; ethion, 563-12-2; fensulfothion, 115-90-2; fonofos, 944-22-9; parathion, 56-38-2; phorate, 298-02-2; allidochlor, 93-71-0; chlorpropham, 101-21-3; linuron, 330-55-2; prometryn, 7287-19-6; trifluralin, 1582-09-8; iprodione, 36734-19-7; total chlordane, 135367-01-0; total endosulfan, 135367-02-1.