Organophosphorus and Organochlorine Pesticide Residues in Italian Citrus Oils

By Giacomo Dugo, Marcello Saitta, Giuseppa Di Bella and Paola Dugo, Università di Messina, Italy

Pesticide residues in citrus oils have been the subject of research since the 1960s. In 1967, Stevens[1] reported the presence of between 1.5 and 20 ppm of organophosphorus pesticides in cold-pressed citrus oils produced in Florida and California. In 1969, Guenther[2] recovered 6-10 ppm of residues in laboratory-produced oils obtained from malathion-treated lemons and oranges, while commercial oils showed 12-450 ppm of parathion. Dupuis[3] reported methidathion levels of 65 ppm in orange oils in 1975.

Until 1987, research on Italian citrus oils was limited to the findings of Leoni et al.[4] Their analyses were carried out by gas chromatography with selective detectors for phosphorated compounds and with an electron-capture detector for chlorinated compounds, after a clean-up procedure that used solvent distribution and column chromatography. All the samples analyzed by Leoni et al. showed residues of ethyl parathion, methyl parathion and their derivatives. Furthermore, malathion was recovered in 52% of the oil samples, fenitrothion in 35% and phenthoate in 29%. It was found that the total organophosphorus pesticide residue levels ranged from 0.74 to 23.28 ppm.

The present work summarizes the results of the qualita-

Table I. Analyzed samples and experimental conditions

Reference	Production years	Samples analyzed	Pesticides analyzed	Injector	Column	Detector
5	1983	33 lemon	organophosphorus	splitter, 250°C	capillary used silica, 25 m x 0.32 mm SE-54, 0.25 µm; 180°C or 230°C[a]	NPD 270°C
6,7	1984-1986	222 lemon 73 sweet orange	organophosphorus	splitter, 250°C	capillary fused silica, 30 m x 0.25 mm DB-5, 0.25 µm; 170°C or 230°C[a]	NPD 270°C
8,9	1990-1992	50 lemon 73 sweet orange 84 mandarin 9 bergamot	organophosphorus	PTV, 65-240°C at 990°C/min	capillary fused silica, 30 m x 0.25 mm SPB-5; 75-170°C (5 min) at 30°C/min; 170-190°C at 2°C/min; 190-265°C at 30°C/min	FPD 250°C
10	1992	129 bergamot	organophosphorus	PTV, 65-240°C at 990°C/min	capillary fised silica, 5 m x 0.25 mm, SE-54 0.25 µm; 75-140°C at 30°C/min; 140-245°C at 5°C/min	FPD 250°C
11	1991-1992	15 lemon 19 sweet orange 11 mandarin 15 bergamot 2 clementine	organochlorine	splitter, 230°C	capillary fused silica, 30 m x 0.25 mm, SPB-5 0.25 µm; 150-230°C at 2°C/min; 230-280°C at 10°C/min	ECD 280°C

[a]230°C was used for determination of methyl azinphos and ethyl azinphos
NPD = nitrogen phosphorus detector; FPD = flame photometric detector; ECD = electron capture detector; PTV = programmed temperature vaporizer

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Table II. Relative retention times (RRT) and detection limits (d.l.) in picograms for organophosphorus pesticides

N	Pesticide	RRT[a] (ref 6,7)	RRT[b] (ref 6,7)	RRT (ref 10)	RRT (ref 8,9)	d.l.[c] (pg)	d.l.[d] (pg)
1	dichlorvos				0.218		9
2	mevinphos			0.317	0.288		18
3	sulfotep	0.38		0.521	0.471	55	5
4	dimethoate	0.43		0.548	0.524	63	22
5	fonofos				0.596		4
6	diazinon	0.54		0.658	0.617	59	4
7	methyl paraoxon				0.629		14
8	methyl parathion	0.71		0.762	0.758	38	5
9	methyl chlorpyriphos				0.761		6
10	ethyl paraoxon				0.802		11
11	fenchlorphos				0.809		5
12	fenitrothion	0.85		0.866	0.854	31	5
13	methyl pirimiphos	0.89		0.893	0.866	31	5
14	malathion	0.95		0.933	0.898	45	5
15	fenthion				0.926		5
16	ethyl chlorpyriphos				0.936		5
17	ethyl parathion	1	1	0.949	0.937	41	5
18	methyl bromophos	1.11		1	1	49	6
19	ethyl pirimiphos				1.032		4
20	chlorfenvinphos				1.103		8
21	phenthoate				1.105		5
22	quinalphos	1.36		1.132	1.109	48	5
23	mecarbam				1.112		5
24	methidathion	1.45		1.172	1.144	54	5
25	ethyl bromophos	1.53		1.211	1.156	57	5
26	iodofenphos				1.198		7
27	ethion				1.274		1
28	methyl azinphos		2.88	2.273	1.423	63	16
29	ethyl azinphos		3.51	2.526	1.475	58	7
30	coumaphos				1.539		13

[a] 170°C; [b] 230°C; [c] NPD; [d] FPD

Table III. Relative retention times (RRT) and detection limits (d.l.) in parts per billion for organochlorine pesticides (SPB-5)

N	Pesticide	RRT (ref 11)	d.l. (ppb)
1	aldrin	0.856	23
2	p,p'-dichlorobenzophenone	0.906	42
3	methyl bromophos (i.s.)	1	-
4	dieldrin	1.291	27
5	p,p'-DDE	1.304	25
6	o,p'-DDD	1.341	45
7	endrin	1.382	27
8	p,p'-DDD	1.494	34
9	o,p'-DDT	1.508	36
10	p,p'-DDT	1.667	31
11	dicofol	1.943	23
12	tetradifon	2.038	14

i.s. = internal standard

tive and quantitative analyses of organophosphorus and organochlorine pesticides in Italian citrus oils produced from 1983 to 1992.

Experimental

The samples analyzed, the analyses performed and the experimental conditions are listed in Table I.

Organophosphorus pesticide residue analyses were carried out directly on oils, without clean-up procedures.[5-10] For the organochlorine pesticide analyses, the samples were purified on silica gel columns using dichlorometh-ane as eluent.[11] For the organophosphorus pesticide analysis, malathion[5-9] on methyl bromophos[6-10] were used as internal standards. For the organochlorine pesticide analysis methyl bromophos was used as the internal standard.[11]

Organophosphorus pesticide residue analyses were carried out on lemon oil (305 samples), sweet orange oil (146 samples), mandarin oil (84 samples) and bergamot oil (138 samples). All oils were of Italian origin and were produced between 1983 and 1992.

Organochlorine pesticide residue analyses were also performed on lemon oil (14 samples), sweet orange oil (19 samples), mandarin oil (11 samples), bergamot oil (14 samples) and clementine oil (2 samples). All oils were of Italian origin and were produced between 1991 and 1992.

Table II shows the organophosphorus pesticides screened, their retention times relative to ethyl parathion and methyl bromophos, and their detection limits with both the nitrogen phosphorus detectors (NPD) and the flame photometric detectors (FPD).

Figure 1 is a chromatogram of a standard mixture of organophosphorus pesticides, obtained with NPD. Figure 2 shows the chromatograms of two standard mixtures of organophosphorus pesticides, obtained with FPD. The pesticides are generally well separated, with the exception of the following couples: methyl parathion and methyl chlorpyriphos, ethyl chlorpyriphos and ethyl parathion, chlorfenvinphos and phenthoate, and quinalphos and mecarbam.

Table III shows the organochlorine pesticides detected, their retention times relative to methyl bromophos and their respective detection limits with electron capture detectors (ECD). Figure 3 is a chromatogram of a standard mixture of organochlorine pesticides.

Organophosphorus Pesticides

Lemon oils: In Figures 4 and 5, the chromatograms of lemon oils obtained with NPD and FPD, respectively, are reported. As these figures show, under the experimental conditions used, the natural components of the essential oils are eluted quickly from the column and appear in the first part of the chromatogram, their peaks being negative with the FPD. The organophosphorus pesticides are located in the second part of the chromatogram.

In Table IV, the organophosphorus pesticide residue values in lemon oils of different production years are listed. This table shows the concentration range of each pesticide,

Table IV. Organophosphorus pesticide residues in lemon oil (ppm)

Production season	1983	1984	1985	1986	1987	1988	1989	1990-1991	All	% of contaminated samples
No. of samples	33	48	39	32	13	57	33	50	305	
sulphotep								0-0.05	0-0.05	0.7
diazinon		0-0.18	0-2.10	0-0.054	0-6.39	0-5.73	0-1.24	0-0.03	0-6.39	29.2
methyl parathion	0.65-39.00	0-20.90	0-10.90	0.30-19.30	0.63-18.90	0-35.00	1.09-13.90	0.01-10.27	0-39.00	97.4
fenitrothion		0-14.50	0-0.18	0-2.77	0-0.09	0-1.56	0-0.21	0-0.48	0-14.50	9.2
methyl pirimiphos								0-0.04	0-0.04	0.7
malathion		0-0.70	0-0.47	0-0.51		0-0.31	0-0.32		0-0.70	3.6
ethyl parathion	trace-12.10	0.09-17.20	0-12.80	0.62-13.00	0-4.02	0.09-16.00	0.66-10.70	0.03-5.42	0-17.20	99.3
quinalphos		0-14.20	0-10.00	0-7.84	0.07-1.76	0-11.00	0-1.48	0-0.39	0-14.20	53.8
methidathion	0-54.00	0.06-48.50	0.11-40.10	3.59-40.00	1.14-105.00	0.37-201.00	1.43-33.60	0.01-11.95	0-201.00	98.4
iodophenphos								0-1.04	0-1.04	0.7
ethyl bromophos				0-2.79					0-2.79	0.3
ethyl azinphos								0-1.73	0-1.73	4.9
Range	2.005-95.10	5.98-48.50	0.65-58.48	4.51-57.00	5.84-130.31	4.39-218.53	7.93-41.20	0.90-17.78	0.40-218.53	100.0
Total content X	27.6	12.8	13.6	35.6	29.0	49.3	25.7	4.95	24.5	

Table V. Organophosphorus pesticide residues in sweet orange oils (ppm)

	Sicilian Oils					Calabrian Oils			
Production season	1989	1991	1992	All	% of contaminated samples	1989	1991	All	% of contaminated samples
No. of samples	42	50	12	104		31	11	42	
sulphotep		0-0.90		0-0.90					
dimetoate	0-0.52	0-0.94		0-0.94	4.8	0-0.45		0-0.45	2.4
diazinon	0-4.28	0-01.05	0-0.30	0-4.28	53.8	0-3.12	0-0.25	0-03.12	33.3
methyl parathion	0-77.20	0.03-14.15	0.34-3.68	0-77.20	98.1	0.04-13.40	0.54-11.55	0.04-13.40	100.0
fenitrothion	0-0.13	0-0.14	0-0.31	0-0.31	10.6				
methyl pirimiphos	0-0.72	0-0.04	0-0.12	0-0.72	5.8	0-0.12		0-0.12	2.4
malathion	0-1.17	0-0.31	0-0.11	0-1.17	12.5	0-2.19		0-2.19	9.5
ethyl parathion	0.55-51.40	0.01-6.82	0.52-9.81	0.01-51.40	100.0	1.71-32.10	0.05-3.54	0.05-32.10	100.0
chlorfenvinphos		0-0.10		0-0.10	1.0				
quinalphos	0-11.18	0.01-2.50	0.08-1.02	0-11.18	81.7		0.01-2.46	0.01-2.46	26.2
methidathion	0-97.20	0.06-10.29	0-6.31	0-97.20	97.1		0.04-5.83	0.04-5.83	26.2
ethyl bromophos	0-12.20		0-2.18	0-12.20	4.8				
ethion			0-0.01	0-0.01	1.9				
methyl azinphos		0-5.95	0-0.28	0-5.95	8.7		0-2.01	0-2.01	2.4
ethyl azinphos		0-0.03		0-0.03	1.0				
Range	2.69-253.96	0.40-24.66	3.37-12.87	0.40-253.96	100.0	3.80-36.20	0.80-16.13	0.80-36.20	100.0
Total content X	17.3	7.7	7.4	11.5		15.0	7.2	13.3	

the percentage of samples contaminated by each pesticide and reports on the total pesticide content. As can be seen, in 1983 all of the samples were contamined with methyl parathion and ethyl parathion, and most of the samples also showed methidathion residues. The total phosphorated ester content that year was in the 2-95 ppm range. Since 1984, quinalphos has been detected in about 50% of samples analyzed, and diazinon in about 30%. Small quantities of fenitrothion, malathion and ethyl bromophos have also occasionally been recovered.

As can be seen from Table IV, the average level of contamination peaked in 1988 and decreased in 1990-1991 to average about 5 ppm. In certain years, the average levels of contamination were affected strongly by the very high levels found in a small number of samples. Figure 6 shows the frequencies of the different pollution levels for the periods 1983-1985, 1986-1988 and 1989-1991. The highest contamination value in the years 1983-1985 (Table IV) was 95.10 ppm, but as can be

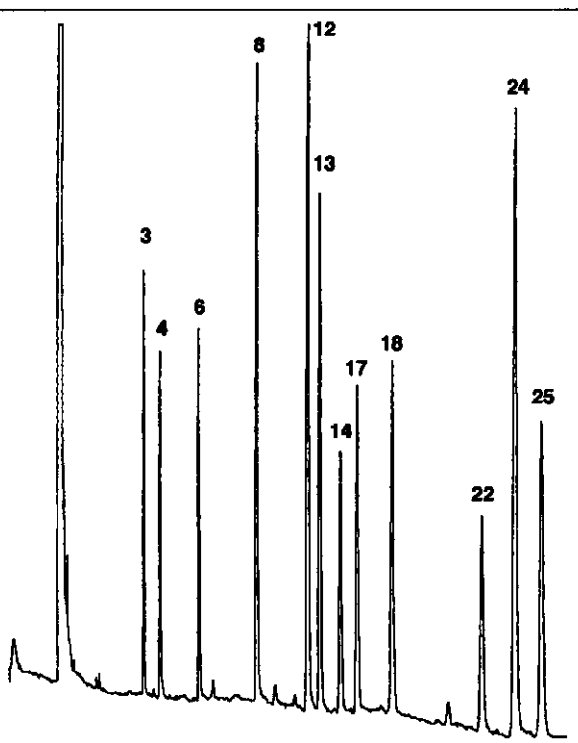

Figure 1. Chromatograms of standard mixtures of organophosphorus pesticides. Column: DB-5, 30 m x 0.25 mm; temperature: 170°C; detector: NPD. For peaks identification, see Table II.

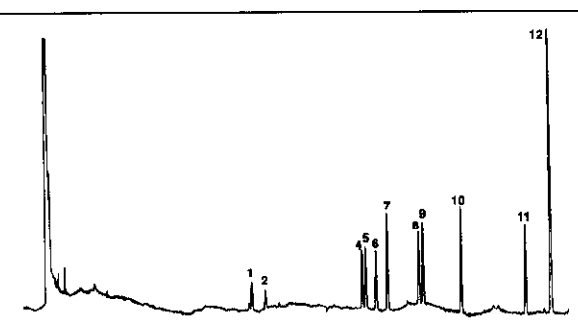

Figure 3. Chromatogram of a standard mixture of organochlorine pesticides
Experimental conditions as reported in Table I.
For peaks identification, see Table II.

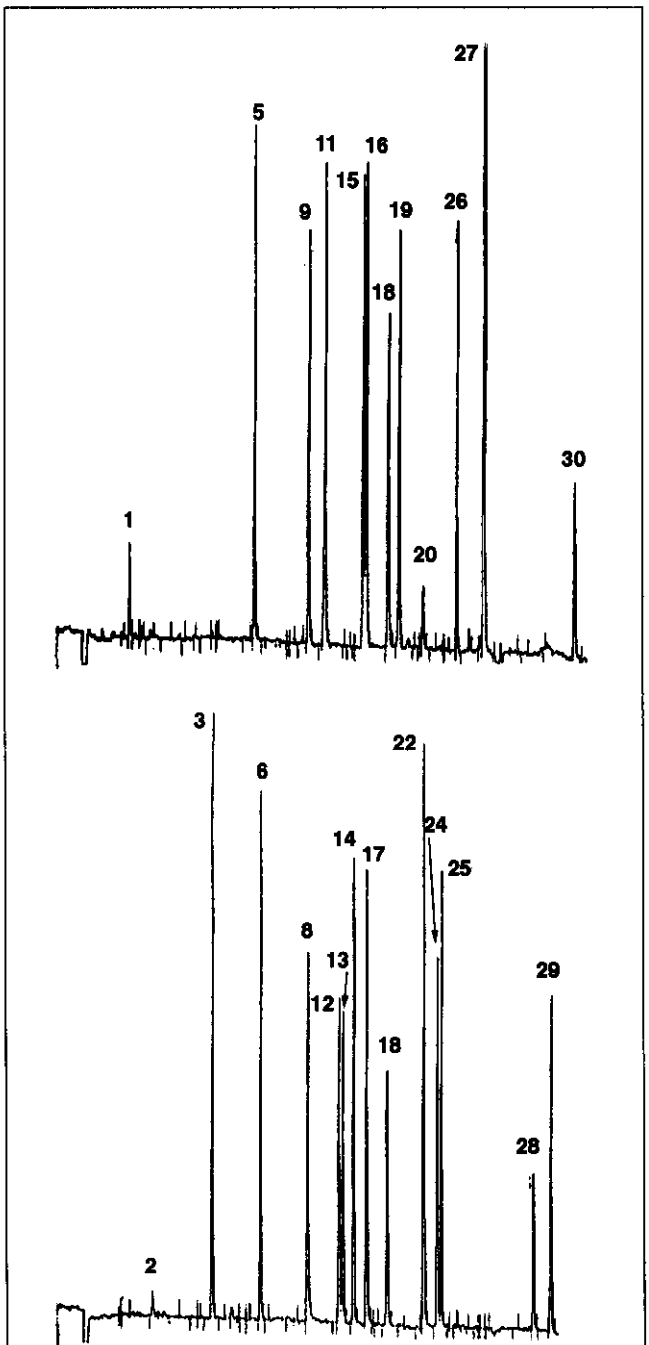

Figure 2. Chromatograms of standard mixtures of organophosphorus pesticides
Column: SPB-5, 30 m x 0.25 mm; temperature: 75° to 170°C (5 min) at 30°C/min, to 190°C at 2°C/min, to 265°C at 30°C/min; detector: FPD.
For peaks identification, see Table II.

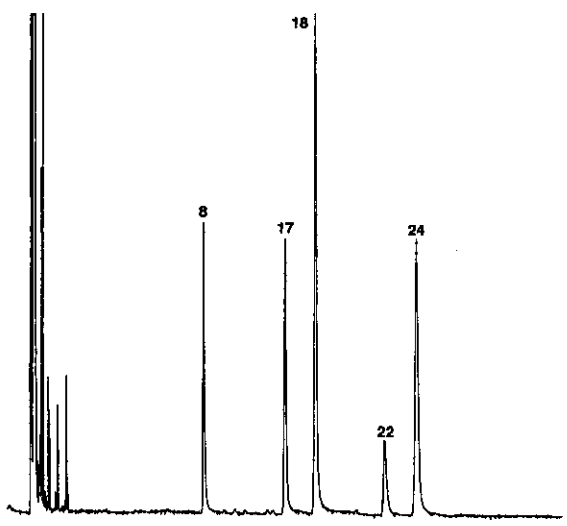

Figure 4. Chromatogram of a lemon oil by NPD Experimental conditions as reported in Figure 1. For peaks identification, see Table II.

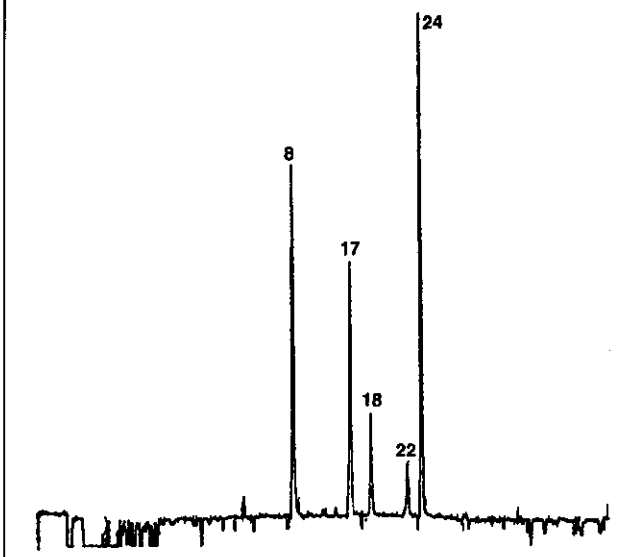

Figure 5. Chromatogram of a lemon oil by FPD Experimental conditions as reported in Figure 2. For peaks identification, see Table II.

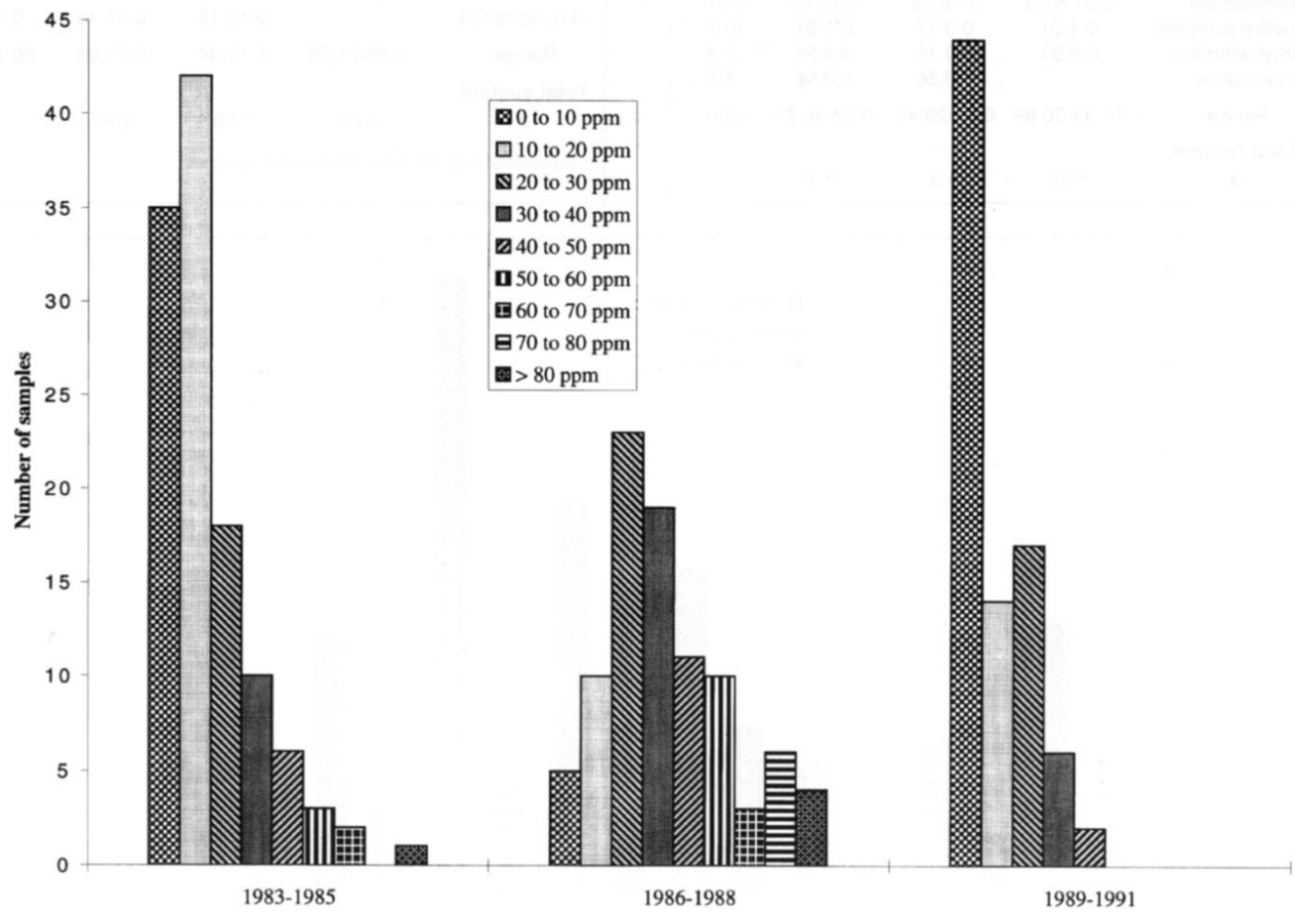

Figure 6. Organophosphorus pesticide residues in lemon oils

seen from the histograms reported in Figure 6, 90% of the samples had a total residue content of less than 60 ppm. Again, in the years 1986-1988, when the highest value was 218.53 ppm, 86% of the samples had a total residue content lower than 60 ppm. Finally, in the years 1989-1991, 90% of the samples had a total residue content lower than 30 ppm. Methidathion was the most predominant of the pesticides detected, as is shown in Figure 7, where the average levels of the main organophosphorus contaminants of lemon oil are compared.

Sweet orange oils: Figure 8 is a sweet orange oil chromatogram obtained with a flame photometric detector. Table V reports the levels of organophosphorus pesticides found in sweet orange oils. Samples are subdivided according to their production year and origin. This table shows the concentration range of each pesticide, the percentage of samples contaminated by each pesticide and reports on the total pesticide content.

In almost all of the Sicilian sweet orange oils, methyl parathion, ethyl parathion, quinalphos and methidathion

Table VI. Organophosphorus pesticide residues in mandarin oils (ppm)

Production season	1990-1991	1992	All	% of contaminated samples
No. of samples	10	74	84	
mevinphos	0-1.28		0-1.28	8.3
sulphotep	0-0.03		0-0.03	1.2
diazinon	0-1.36	0-0.48	0-1.36	10.7
methyl parathion	7.10-14.74	0-17.39	0-17.39	88.1
fenitrothion		0-1.13	0-1.13	8.3
malathion		0-0.96	0-0.96	7.1
ethyl parathion	1.97-17.74	0-13.35	0-17.74	95.2
phentoate		0-1.26	0-1.26	1.2
quinalphos	0-1.04	0-1.42	0-1.42	50.0
mecarbam		0-8.92	0-8.92	5.9
methidathion	0.31-6.03	0-16.02	0-16.02	91.7
methyl azinphos	0-1.01	0-0.77	0-1.01	10.7
ethyl azinphos	0-0.56	0-0.16	0-0.56	2.4
coumaphos		0-0.56	0-0.56	8.3
Range	14.93-36.89	0.82-28.43	0.82-36.89	100.0
Total content				
X	19.5	9.9	11.0	

Table VII. Organophosphorus pesticide residues in bergamot oils (ppm)

Production season	1991	1992	All	% of contaminated samples
No. of samples	9	129	138	
mevinphos	0.01-0.89		0.01-0.89	6.5
sulphotep	0-0.43		0-0.43	1.4
diazinon	0-0.15	0-0.17	0-0.17	1.4
methyl parathion	0-19.75	0-17.85	0-19.75	18.1
fenitrothion		0-1.19	0-1.19	0.7
malathion	0-0.03		0-0.03	0.7
ethyl parathion	0-6.83	0-2.23	0-6.83	20.3
phentoate		0-1.26	0-1.26	1.2
quinalphos	0-4.58	0-0.22	0-4.58	9.4
methidathion	0-0.66	0-19.44	0-19.44	25.4
ethyl azinphos		0-11.15	0-11.15	0.7
Range	0.88-21.08	0-19.44	0-21.08	50.7
Total content				
X[a]	5.68	2.68	2.89	

[a] Calculated only for the contaminated samples

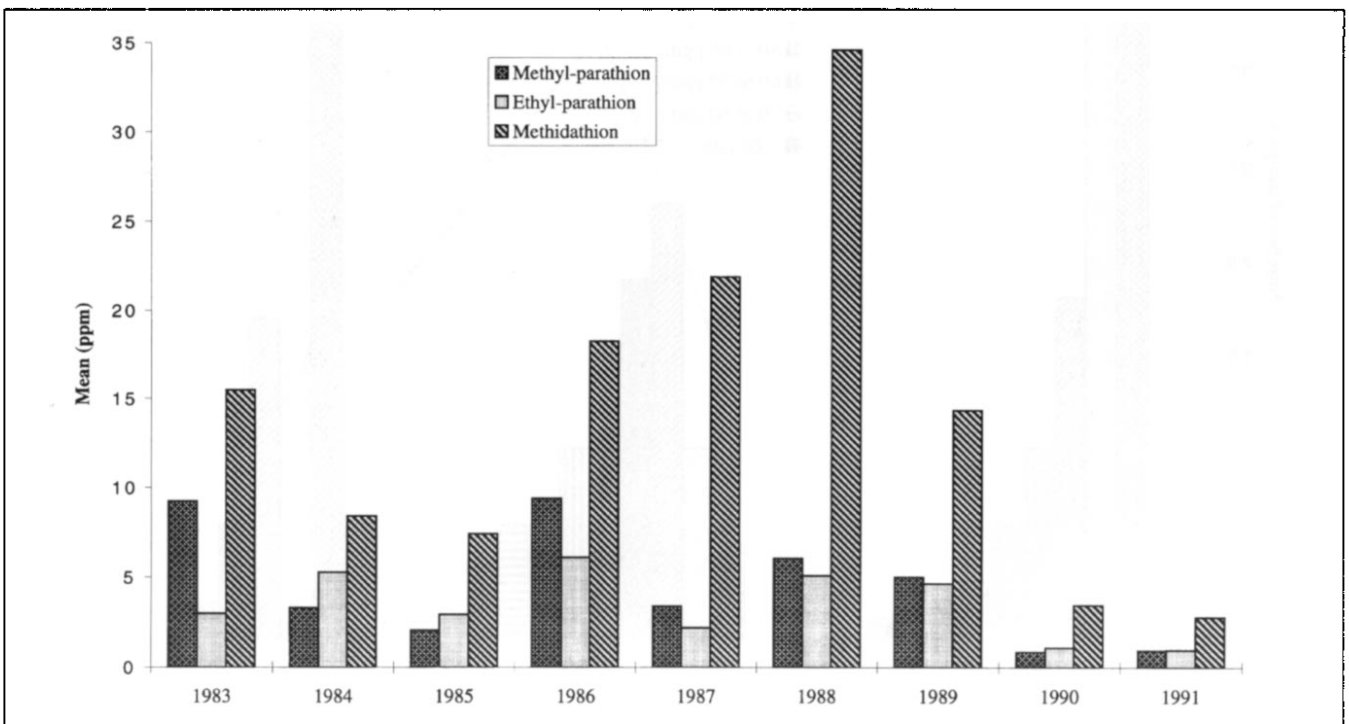

Figure 7. Average values of methyl parathion, ethyl parathion and methidathion in lemon oils

were contemporaneously recovered and, in 50% of the samples, diazinon also was found. The contribution of methidathion to the total phosphorated ester content was about 50%.

All of the Calabrian oils showed residues of methyl parathion and ethyl parathion, while the presence of methidathion, quinalphos and diazinon was less frequent compared to the Sicilian oils. Figure 9 compares the average values of contamination from the main organophosphorus contaminants in Sicilian and Calabrian oils. In any given year, the total average pesticide contents were very similar for Calabrian and Sicilian oils. Oils produced in 1991 and 1992 were less contamined compared to the 1989 oils, and this confirms the trend observed for lemon oils.

The frequencies of the different contamination levels can be seen in Figure 10, which shows that although the highest value of organophosphorus pesticides was 254 ppm (Table V), levels higher than 30 ppm were found in only three samples.

Mandarin oils: Figure 11 shows an FPD chromatogram of a mandarin oil. The levels of organophosphorus pesticides found in mandarin oils are listed in Table VI. The table shows the concentration range of each pesticide, the

Table VIII. Organochlorine pesticide residues in citrus oils (ppm)

Oil	Samples and pesticides	Sicilian	Calabrian	Combined	% of Contaminated samples
lemon	number of samples	6	8	14	
	p,p'-dichlorobenzophenone	0.48-2.74	0-3.19	0-3.19	92.8
	dicofol	0.05-4.80	0-3.47	0-4.80	92.8
	tetradiphon	0.02-2.56	0-1.02	0-2.56	92.8
Range		0.55-9.57	0-7.23	0-9.57	92.8
Total content X		5.8	4.3	5.0	
sweet orange	number of samples	11	8	19	
	p,p'-dichlorobenzophenone	0.51-5.48	0-4.01	0-5.48	94.7
	dicofol	0.28-5.02	0-3.33	0-5.02	94.7
	tetradiphon	0.14-2.15	0-1.25	0-2.15	94.7
Range		1.53-12.65	0-8.25	0-12.65	94.7
Total content X		5.3	4.2	4.8	
mandarin	number of samples	8	3	11	
	p,p'-dichlorobenzophenone	0-6.64	0-2.49	0-6.64	81.8
	dicofol	0-5.83	0.12-2.12	0-5.83	90.9
	tetradiphon	0.05-2.98	0.03-1.03	0.03-2.98	100.0
Range		0.05-15.45	0.23-5.64	0.05-15.45	100.0
Total content X		4.9	2.0	4.2	
bergamot	number of samples		14		
	p,p'-dichlorobenzophenone		0-1.19		42.9
	dicofol		0-0.60		50.0
	tetradiphon		0-0.22		35.7
Total content			0-1.44		50.0
clementine	number of samples	2			
	p,p'-dichlorobenzophenone	0-9.83			50.0
	dicofol	0-1.49			50.0
	tetradiphon	0-3.48			50.0
Total content		0-14.8			50.0

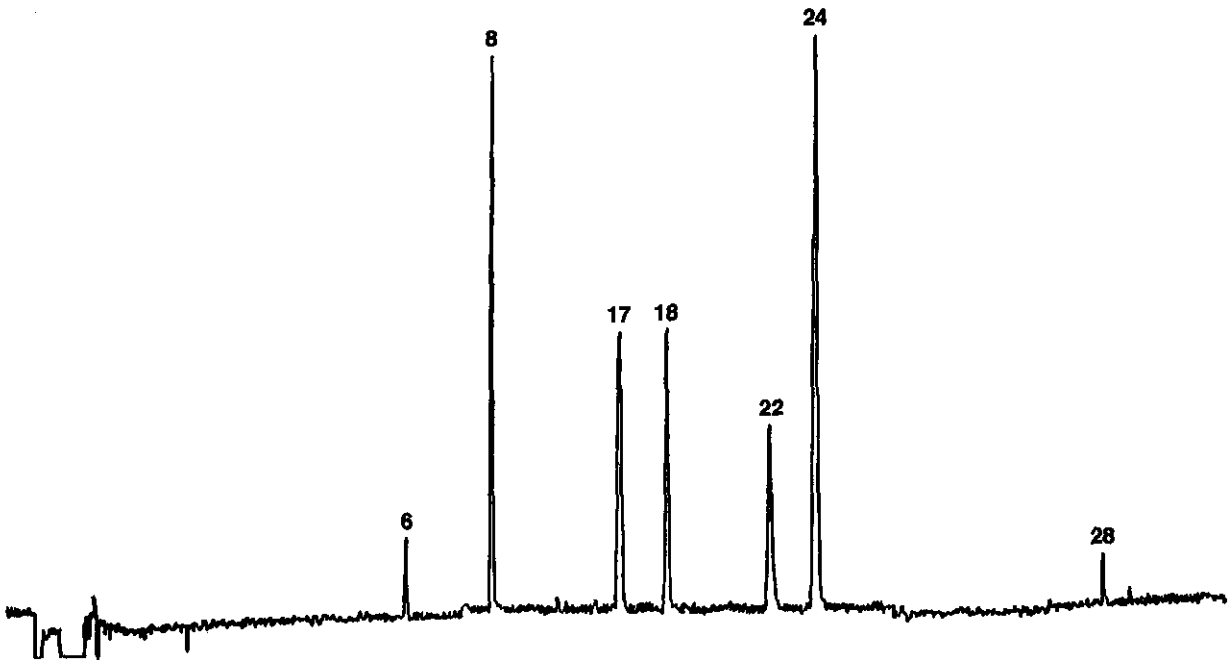

Figure 8. Chromatogram of a sweet orange oil by FPD. Experimental conditions as reported in Figure 2. For peaks identification, see Table II

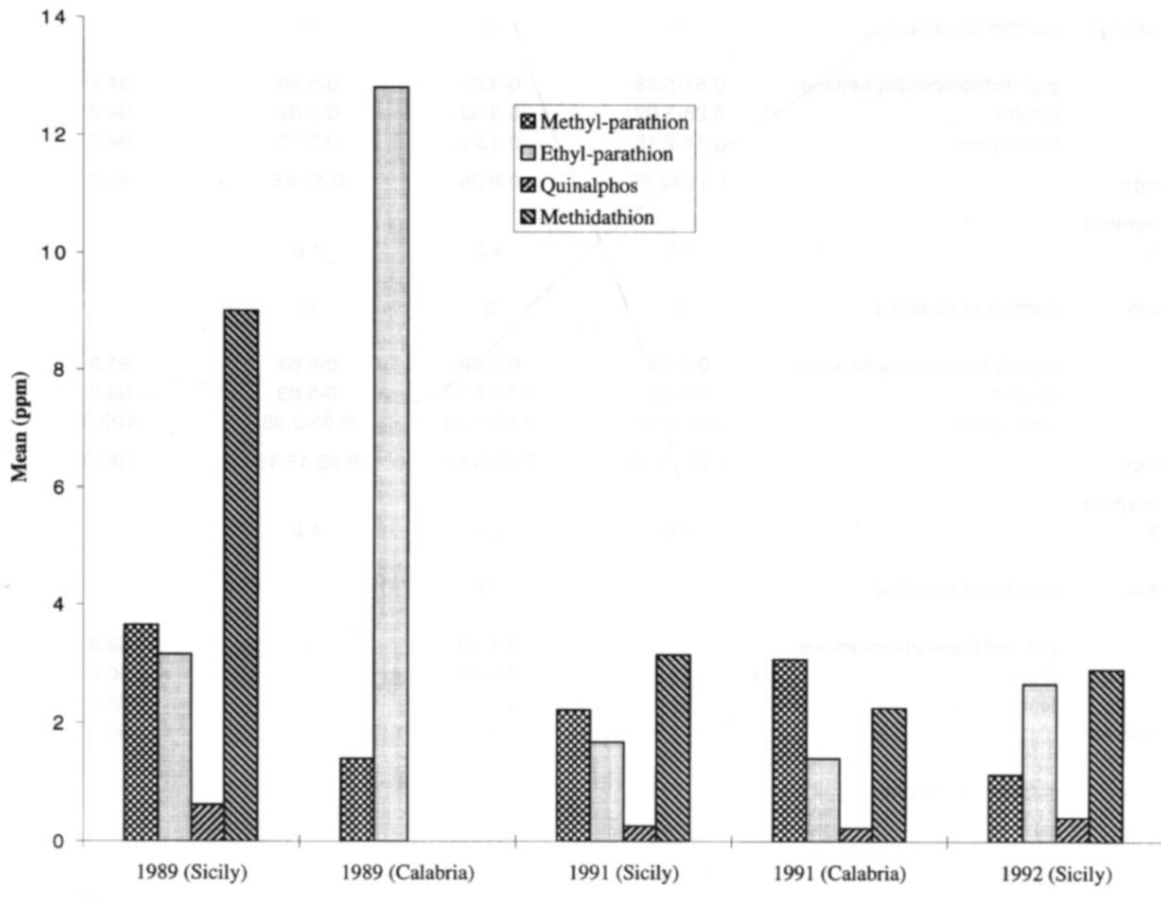

Figure 9. Average values of methyl parathion, ethyl parathion, quinalphos and methidathion in sweet orange oils from Sicily and Calabria

percentage of samples contaminated by each pesticide and reports on the total pesticide content. In almost all the samples, methyl parathion, ethyl parathion and methidathion were found together. In 50% of the samples, quinalphos was recovered. Mevinphos, frequently found in 1990-1991 samples, was not recovered from 1992 oils. In the 1992 oils, phenthoate, mecarbam and coumaphos occasionally were

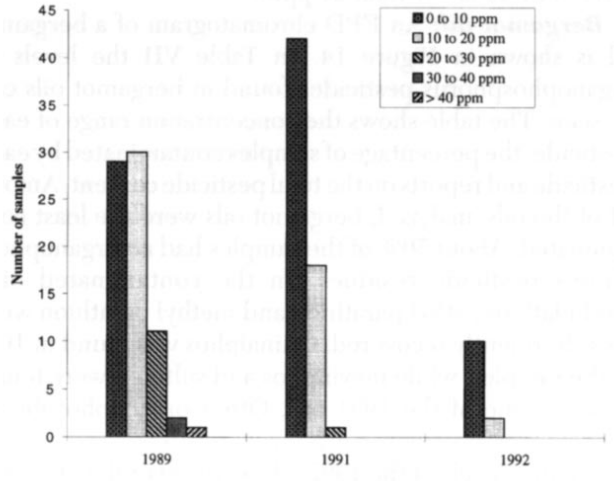

Figure 10. Organophosphorus pesticide residues in sweet orange oils

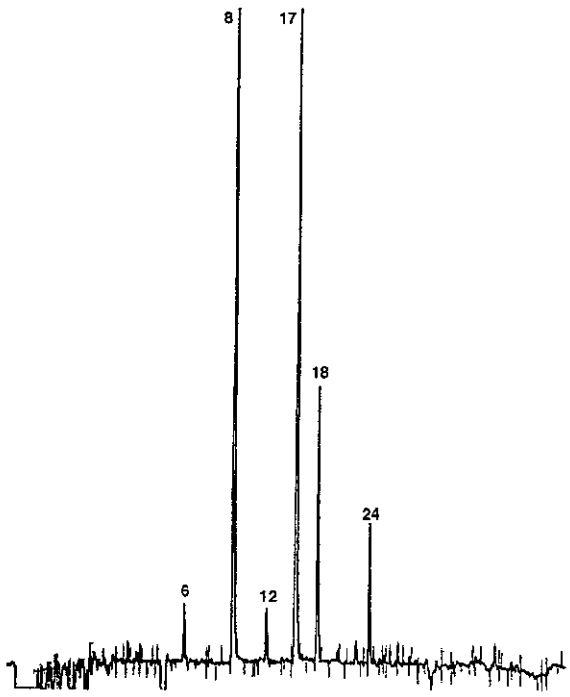

Figure 11. Chromatogram of a mandarin oil by FPD Experimental conditions as reported in Figure 2. For peaks identification, see Table II

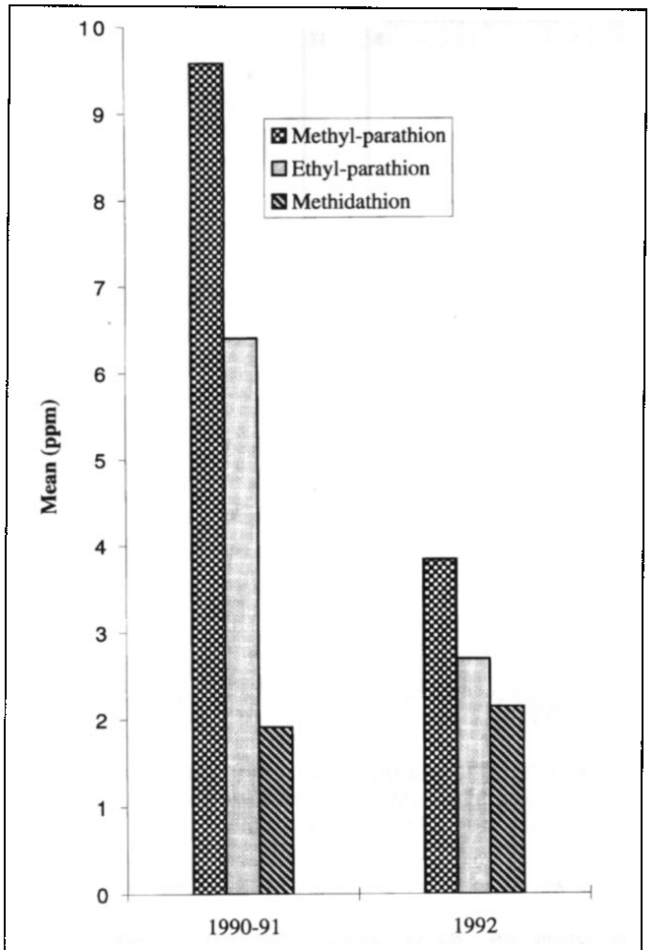

Figure 12. Average values of methyl parathion, ethyl parathion and methidathion in mandarin oils

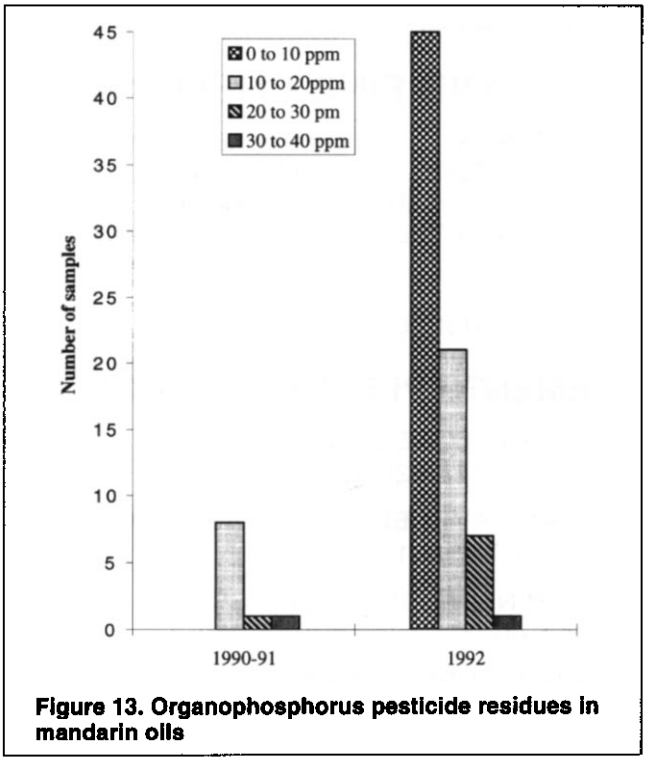

Figure 13. Organophosphorus pesticide residues in mandarin oils

found. These pesticides were not detected in 1990-1991 oils or in any of the other citrus oils analyzed. The average pesticide residue level for oils produced in 1992 was about half that of the previous two years. The average values of the main organophosphorus contaminants and the frequencies of the different contamination levels can be seen in Figures 12 and 13 respectively. It is possible to see from Figure 13 that 88% of the samples had a phosphorated ester content lower than 20 ppm.

Bergamot oil: An FPD chromatogram of a bergamot oil is shown in Figure 14. In Table VII the levels of organophosphorus pesticides found in bergamot oils can be seen. The table shows the concentration range of each pesticide, the percentage of samples contaminated by each pesticide and reports on the total pesticide content. Among all of the oils analyzed, bergamot oils were the least contaminated. About 50% of the samples had no organophosphorus pesticide residues. In the contaminated oils, methidathion, ethyl parathion and methyl parathion were most frequently recovered. Quinalphos was found in 10% of the samples, while mevinphos and sulfotep were found in only some of the 1991 oils. Other organophosphorus pesticides occasionally were recovered. The average contamination levels of the 1992 oils were lower than those of the previous year. Figure 15 shows the average values of the main organophosphorus contaminants, and Figure 16 the frequencies of the different contamination levels. As can be seen from Figure 16, 93% of the samples showed a phosphorated ester content lower than 10 ppm.

Chlorinated Pesticides

The ECD chromatograms of lemon, orange, mandarin and bergamot oils can be seen in Figures 17-20 respectively. Data on the content of organochlorine pesticides in all of the examined oils are reported in Table VIII. The table shows the concentration range of each pesticide, the percentage of samples contaminated by each pesticide and reports on the total pesticide content. Almost all the samples showed the presence of dicofol, tetradifon and p,p'-dichlorobenzophenone, a decomposition product of dicofol. Other organochlorine compounds were not detected.

Of the 14 lemon oils analyzed, 13 were contaminated. The highest total value of organochlorine pesticides was 9.57 ppm. Sicilian oil had a slightly higher average pesticide residue level than Calabrian oils.

All but one of the 19 sweet orange oils that were analyzed were contaminated. The highest total value of organochlorine pesticides was 12.65 ppm. In about 72% of the samples, the p,p'-dichlorobenzophenone residue was higher than that of dicofol. This suggests that the dicofol used on the trees was partially decomposed. The average pesticide content in sweet orange oils was higher in Sicilian than in Calabrian oils, as it had been with lemon oils.

All 11 mandarin oils that were analyzed showed organochlorine pesticide residues, although in one sample, the contamination was only 0.05 ppm of tetradiphon. The highest concentration of organochlorine pesticides was 15.45 ppm. Once again, Sicilian oils showed higher levels

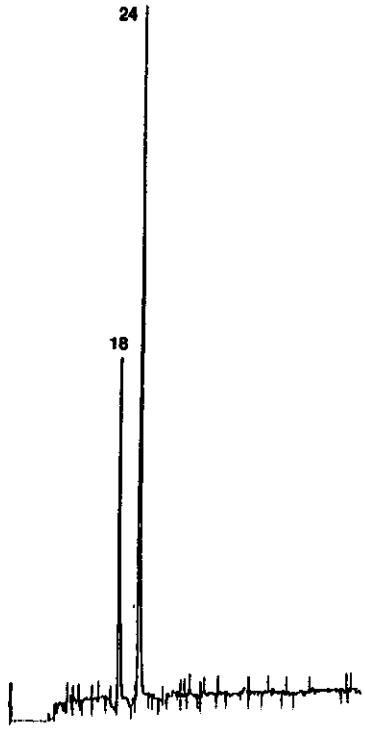

Figure 14. Chromatogram of a bergamot oil by FPD
Column: SE-54, 5 m x 0.25 mm; temperature: 75° to 140°C at 30°C/min, to 245°C at 5°C/min; detector: FPD.
For peaks identification, see Table II.

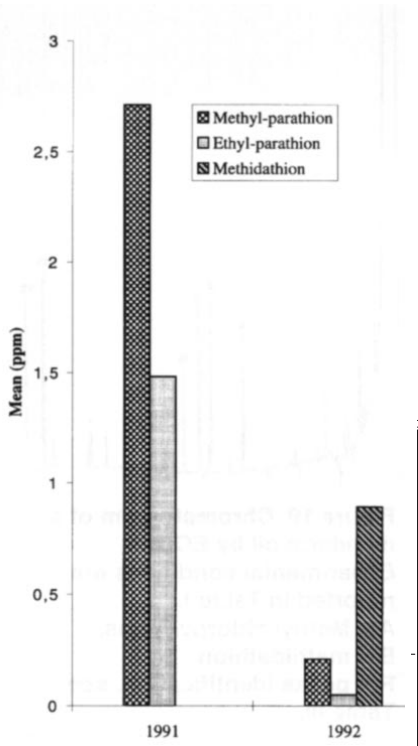

Figure 15. Average values of methyl parathion, ethyl parathion and methidathion in bergamot oils

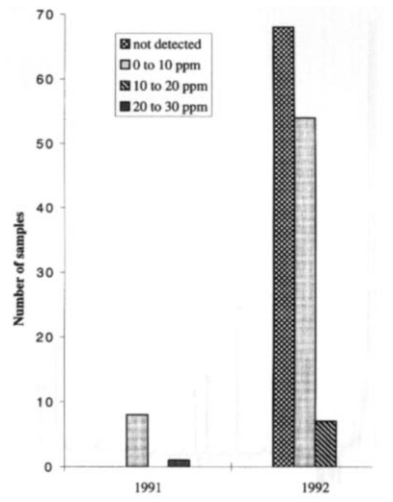

Figure 16. Organophosphorus pesticide residues in bergamot oils

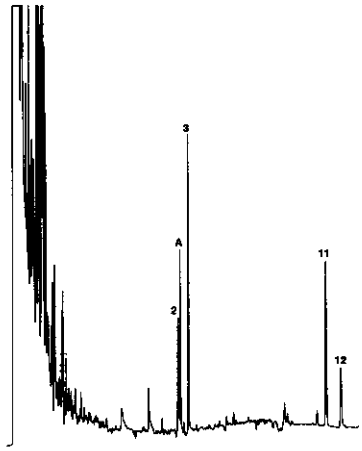

Figure 17. Chromatogram of a lemon oil by ECD
Experimental conditions are reported in Table I.
A = Methyl chlorpyriphos
For peaks identification, see Table III.

of contamination than Calabrian ones.

In addition to possessing the lowest levels of organophosphorus contamination, bergamot oils also showed lower levels of organochlorine pesticides compared to other citrus oils. Of the samples examined, only 50% were contaminated, and the highest organochlorine pesticide content was 1.44 ppm.

In regard to the two clementine oils analyzed, one was a biological sample in which organochlorine pesticides were not detected, while the other showed a residue content of 14.8 ppm.

Summary

From these results, the following observations can be made:

- Methyl parathion, ethyl parathion and methidathion are the most widely used pesticides in citrus cultivation in Italy.
- The pesticides quinalphos, dicophol and tetradifon also are frequently used.
- Methidathion is the insecticide that is found in the largest quantities in lemon oils.
- The insecticides most frequently detected in sweet orange oils are methyl parathion and ethyl parathion. In Sicilian oils, methidathion and quinalphos also are found.
- The insecticides most commonly found in mandarin oils are methyl parathion, ethyl parathion and methidathion. The average contamination values for mandarin oils were higher in comparison with lemon and orange oils for the same years. It is possible to correlate these data with the lower resistance of mandarin fruits to insect attack, and the greater need for pesticide treatments compared to the other citrus fruits.
- Bergamot oils showed the lowest contamination levels. Contaminated oils made up about 50% of the samples analyzed, and the pattern of contamination seemed occasional, not repetitive. These data probably are connected to the strong resistance of bergamot fruits to insect attack, and the reduced use of pesticides compared to the use on other citrus fruits.
- The pesticide residue level in Italian citrus oils has shown a measurable decrease since 1988.

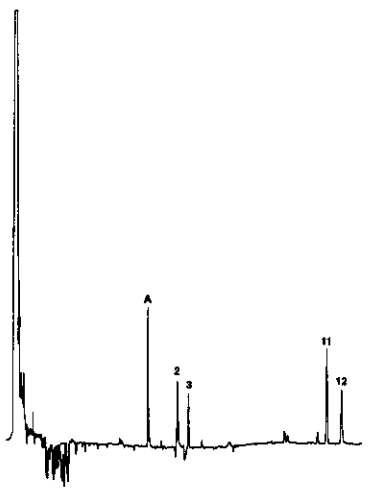

Figure 18. Chromatogram of a sweet orange oil by ECD Experimental conditions are reported in Table I. A = Methyl chlorpyriphos For peaks identification, see Table III

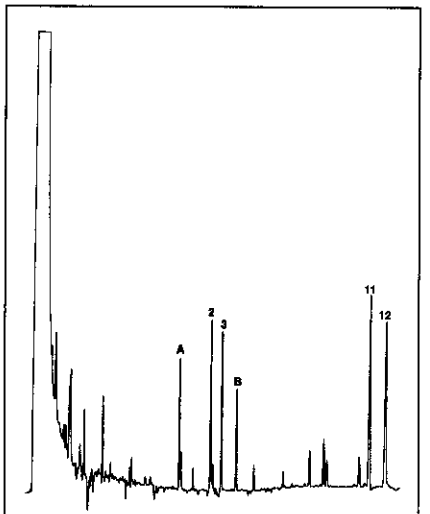

Figure 19. Chromatogram of a mandarin oil by ECD Experimental conditions are reported in Table I. A = Methyl chlorpyriphos, B = methidathion For peaks identification, see Table III.

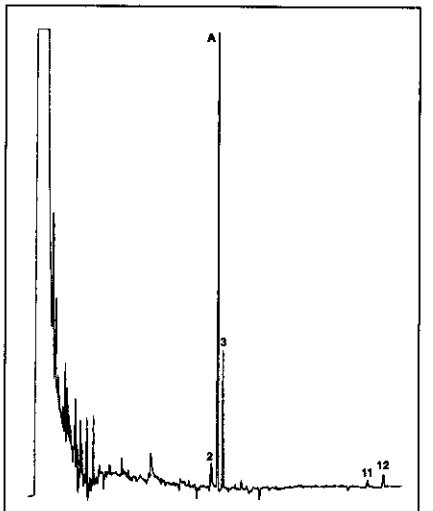

Figure 20. Chromatogram of a bergamot oil by ECD Experimental conditions are reported in Table I. A = Methyl chlorpyriphos For peaks identification, see Table III.

This suggests that there is a trend toward reduction and rational use of pesticide treatments, which in the past were sometimes applied more liberally than the occasion warranted.

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Address correspondence to Paola Dugo, Dipartimento Farmaco-chimico, Facoltà di Farmacia, Università di Messina, 98168 Messina, Italy.

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