HDC Project FV43

Final Report

by

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October 1991

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Carrots: Accelerated Degradation of Soil Insecticides Applied to Control Carrot Fly

INTRODUCTION

The phenomenon of accelerated degradation of pesticides in previously-treated soils has been recognised for some years. However, it is only during the past decade that its impact on the field performance of soil-applied insecticides in the UK has been recognised. Extensive studies with methyl carbamate insecticides at Horticulture Research International, Wellesbourne (HRI-W) have shown that, after a single application of the recommended dose of some compounds, it may be several years before efficacy is restored to its original level. Some organophosphorus insecticides also have been shown to be susceptible to accelerated degradation in previously-treated soils. Preliminary laboratory studies of soils from carrot-growing regions in Lancashire and East Anglia have revealed that the behaviour of phorate and its principal toxic oxidation products in some of these soils is significantly different from that reported 15-20 years ago.

For more than 20 years, the application of the organophosphorus insecticide phorate at sowing time has remained the most widely-used treatment for carrot fly control in the UK. It has been particularly effective in organic soils, often protecting early and main crop carrots for several months after sowing. However, reports of its reduced efficacy, together with recent evidence of its reduced stability, suggest that its field performance is now being limited by the accelerated degradation of its residues in some soils. Similarly, in view of the widespread use of carbofuran to control a range of pests on many crops (including carrots), the ready induction and prolonged stability of anti-carbofuran activity in some soils would also seem to present a challenge to the continued effectiveness of this insecticide against carrot fly.

Studies were therefore undertaken to:-

1. Establish, under controlled laboratory conditions, the persistence and behaviour of freshly-applied carbofuran and phorate in soils treated previously with the recommended doses of these insecticides.

2. Correlate these stabilities with the frequency of, and intervals between, treatments with these and with other pesticides.

3. Present, on the basis of these results, strategies for limiting the effects of accelerated degradation of soil insecticides on carrot fly control.

The work with carbofuran was done by Mr D Eagle at ADAS Cambridge and the phorate studies were done by Mr D Suett at HRI-W.

EXPERIMENTAL

Carbofuran studies

Samples of soil for determination of carbofuran degradation rate were obtained from 15 fields on typical carrot land in Norfolk. From eight of the fields, samples were also obtained from areas around the margin believed not to have been treated with pesticides. At one of the sites the soil was a peat; all the others were on sandy soils. Details of soil-applied insecticides and nematicide treatments and Fubol treatments are shown in Table 1. Also included are soil type, soil pH and details of blight sprays with ofurace applied to potato crops grown in rotation, because the large number of sprays could have resulted in significant amounts of fungicide reaching the soil.

The method used to test for accelerated degradation of carbofuran was a modification of the technique described by Chapman *et al.* (1985). A 5 g sample of soil was incubated with 0.2 mg of carbofuran in 200 ml of nutrient solution at 30°C in a 500 ml bottle loosely stoppered with a glass wool plug. The nutrient solution contained 1 g potassium dihydrogen phosphate, 1 g dipotassium hydrogen phosphate and 1 g ammonium nitrate per litre. The mixture was thoroughly shaken every second day. A 10 ml aliquot was extracted on the first day and then 7 days later. After centrifuging, the amount of carbofuran present was determined by reverse phase high pressure liquid chromatography using an ultra-violet detector.

<u>Phorate studies</u>

Soils which had been treated with phorate at some time during the last 10 years, were identified. Samples were taken from each of 27 sites on 7 or 26 September 1990. A further 5 samples were taken on 7 September 1990 from untreated gateway areas. At each site approximately 20 x 100g sub-samples were taken randomly with a hand trowel to a depth of 10-15 cm. Samples were mixed by sieving, a sub-sample was removed for determination of soil properties (pH, organic matter and moisture-holding values) and the soils were stored at 2°C. Soil moisture contents at a fixed membrane pressure of 33 kPa were determined: these values were equivalent to approximately 70% of soil moisture-holding capacity.

Before treating with phorate, soils were dried to approximately 50% of their moisture-holding capacities and their moisture contents were determined accurately. Phorate was then applied at a dose equivalent to 10 mg/kg dry soil by adding portions of Fullers Earth microgranules which had been fortified with an acetone solution containing technical phorate (85% a.i.). Further water was added to adjust the water content of each soil to the appropriate value at 33 kPa and, after a short equilibration period, each soil was mixed thoroughly. Duplicate portions were transferred to wide-necked plastic containers, initial samples were taken and the soils were incubated in the dark at 15°C. Moisture contents were maintained and samples were taken for analysis 1, 2, 3, 4, 6, 8 and 12 weeks after treatment.

Phorate residues were extracted with hexane:acetone (4:1), extracts were washed acetone-free, dried and analysed by gas-liquid chromatography.

RESULTS

Carbofuran studies

The percentage degradation of carbofuran in soil samples obtained from the eight areas reported to have been untreated with agrochemicals in recent years ranged generally from 10 to 16% and at one peat site it was 23%. However, at two of the sites, percentages of 38 and 57 were recorded, suggesting that there was probably some treatment effect because previous studies at Cambridge were shown that the percentage degradation in a soil unaffected by accelerated degradation rarely exceeds about 20%. When more than 20% degrades, an enhanced degradation effect usually can be deduced although the significance of this to carrot fly control is not clear unless the degradation approaches 100%, when failure must be likely.

There was clear evidence of accelerated degradation at all except one of the sites where carbofuran or carbosulfan was applied in 1990. Excluding this anomalous site, the effect was least evident (64% on a loamy sand and 38% on a peat) where a carbamate had not been applied for at least three years. Degradation was greatest (100%) where a carbamate had been applied twice during the previous three years and 72-95% when there was a single application. Except for the anomalous site there was a clear tendency for the most intensive carbamate use to cause the greatest enhancement in degradation. The reason for the anomalous behaviour of the soil from the Larks Heath site is not known but may reflect microbiological variability since, in texture and other properties such as pH, it was very similar to the other sandy sites.

Where carbofuran was applied most recently, i.e. in 1989, pronounced enhanced degradation effects were evident at two sites, with degradation of 85% and 96%. The third site was somewhat anomalous with only 48% degradation even though carbofuran had been applied in 1988 as well as 1989. Again there was no apparent reason for this site behaving differently. Degradation was not enhanced at the site where carbofuran had been applied only in 1988 and was enhanced only slightly (32%) where it had been applied only in 1987 or in 1986 (35%).

At the Thornton loamy sand site, degradation was moderately enhanced (45% compared to 16% in the untreated area) even though there had been no application of carbofuran or a similar carbamate during the period 1986-90 for which records are available. Aldicarb was applied in 1986 but it is very unlikely that the effect can be attributed to this alone. The fungicide Patafol Plus was applied seven times to the 1990 potato crop. This contains the active ingredient ofurace which is structurally related to metalaxyl and it is possible that residues of the ofurance sprays applied frequently during the summer had induced activation.

With the exception of the single peat site and the continuous rye field, both of which were pH 6.1, pH's ranged only from 6.9 to 7.4. It was not possible, therefore, to establish a relationship between soil pH and the occurrence of accelerated degradation. Similarly, there was no evidence that applications of Fubol induced the accelerated degradation of carbofuran, since such an effect would have enhanced the somewhat limited degradation which occurred in Gun Breck and Dunwick fields.

Phorate studies

The rates of loss of freshly-applied phorate, expressed as total phorate residues, from the 32 soils studied are shown in Table 2. The total residue comprised parent phorate (P) and its two major oxidation products in soil, namely phorate sulphoxide (PSO) and phorate sulphone (PSO_2). It has long been recognised that the prolonged bio-activity of phorate in soil is due largely to the formation and persistence of PSO and, especially, PSO_2 and the Figures show differences in the composition of these residue components in the different soils.

The results showed that:-

1. Initial half-lives - the time taken for 50% of the initially-applied amount to disappear - ranged from 1 week (soils 1 and 2) to more than 16 weeks (soils 6-10).

2. There was no consistent correlation between degradation rate and previous treatment history. Irrespective of the frequency of previous treatments, initial half-lives of 5 weeks or less were obtained in 17 of the 26 previously-treated soils. In contrast, 5 of the 6 previously-untreated soils showed initial half-lives of 9 weeks or more.

3. Direct comparison of previously-treated and previously-untreated soils at 5 sites (soils 1-5) showed that degradation was much more rapid in 4 of the 5 previously-treated soils. Initial half-lives in these soils ranged from 1-6 weeks compared with 9-11 weeks in the corresponding untreated soils taken from gateways.

4. There was evidence of an association between degradation rate and soil pH (Table 3a). Thus 18 of the previously-treated soils had a pH of 7.4 or more and, in 14 of these, initial half-lives were 4 weeks or less. In contrast, all 8 of the soils with pH less than 7.4 showed half-lives longer than 4 weeks. Furthermore, 5 of the 6 previously untreated soils had a pH of 7.4 or more and in 4 of these soils half-lives exceeded 4 weeks, suggesting that this association between soil pH and phorate degradation did not result solely from the direct effect of pH on insecticide stability.

5. There were indications, in the previously-treated soils, of a possible association between degradation rate and organic matter content (Table 3b). Of the 26 previously-treated soils, 19 had an organic content greater than 10% and 12 of these showed initial half-lives longer than 4 weeks. In contrast, all 7 of the soils with an organic content less than 10% showed initial half-lives of less than 4 weeks. However, it should be noted that all 7 of these soils also had a pH of 8 or more.

6. The behaviour of the individual residue components differed greatly in the different soils. In all 6 of the previously-untreated soils, PSO_2 became, and remained, the major residue component. It commonly reached a level equivalent to 70-80% of the initially-applied dose of phorate, a pattern of behaviour observed in these soils more than 20 years ago. In the previously-treated soils, however, where there were many differences in residue behaviour, rapid loss of total phorate residues was associated generally with the relative instability of PSO and, especially, PSO_2. Thus, in most of the 9 soils which showed greatest degradation (soils 1, 2, 11-13, 20, 21, 24 and 25) PSO reached peak levels after no more than 1 week after treatment and PSO_2 rarely comprised more than 10% of the initial dose.

CONCLUSIONS

<u>Carbofuran studies</u>

The study confirmed that even a single application of carbofuran or carbosulfan is likely to accelerate the degradation of carbofuran in the soils studied. Application in two successive years usually caused even more rapid degradation, making it unlikely that carbofuran or carbosulfan would give effective pest control in at least the next crops. However, while most soils were subject to accelerated degradation there were exceptions which could not be predicted without analysis.

There was no evidence that Fubol applications to carrots affected carbofuran degradation but there was an indication that frequent sprays of ofurace for blight control in potatoes might have had some effect.

Phorate studies

1. It is evident that many carrot growing soils have developed the ability to degrade phorate rapidly.

2. In approximately a third of the previously-treated soils studied, degradation was so rapid that it seems unlikely that phorate could have contributed anything to carrot fly control.

3. In a further third of the soils control of first generation and perhaps early second generation larvae would probably have been achieved.

4. In approximately a third of these soils, phorate persisted long enough to suggest that prolonged control of second generation larvae could have been achieved.

5. Under the right conditions, accelerated degradation of phorate can be stimulated by a single application of the recommended dose.

6. This stimulation occurs most readily in soils with a high pH (> pH 7.5) and least readily in soils with low pH and high organic matter content.

7. Although no correlation could be established between phorate stability and treatment history, the phenomenon is stimulated readily enough to suggest that:

   i) phorate should <u>never</u> be applied to the same soil in successive years;

   ii) crop, and chemical, rotations should be maximised, especially on mineral soils with high pH.

REFERENCE

Chapman, R.A., Moy, P. and Henning, K. (1985). A simple test for adaptation of soil microorganisms to the degradation of the insecticides carbofuran. *Journal of Environmental Science and Health B20*, 313-319.

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Table 1: Carbofuran study. Pesticide treatment histories, soil properties and carbofuran degradation results in 23 soils

Field name/ sampling date/ soil type/ pH		1986	1987	1988	1989	1990	Carbofuran degradation (%)
Thornton 20-8-90 loamy sand 7.3	crop insecticide/nematicide fungicide treated area untreated area	sugar beet aldicarb -	wheat - -	barley - -	peas - -	potatoes - Patafol Plus x 7	 45 16
Rushford 20-8-90 loamy sand 6.9	crop insecticide/nematicide fungicide treated area untreated area		carrots carbofuran Fubol	barley - -	potatoes aldicarb mancozeb x 7	sugar beet carbosulfan -	 95 57
Southgate 22-8-90 loamy sand 7.2	crop insecticide/nematicide fungicide treated area untreated area		oilseed rape - -	barley - -	barley - -	sugar beet carbosulfan -	 64 38
Pauls 13-9-90 loamy sand 6.1	crop insecticide/nematicide fungicide treated area untreated area	rye - -	rye - -	rye - -	rye - -	rye - -	 11 12
Blade Breck 24-9-90 loamy sand 7.2	crop insecticide/nematicide fungicide treated area	lucerne - -	lucerne - -	barley - -	carrot carbofuran Fubol	fallow - -	 96
Tower Heath 24-9-90 loamy sand 7.4	crop insecticide/nematicide fungicide treated area	grass - -	barley - -	parsnip carbofuran -	turnip carbosulfan -	carrot carbofuran Fubol	 100
Gun Breck 24-9-90 loamy sand 7.1	crop insecticide/nematicide fungicide treated area	turnip carbosulfan -	barley - -	parnsip carbofuran -	carrot carbofuran Fubol	Brussels sprout - -	 48

Table 1: continued

Lordships 24-9-90 loamy sand 7.4	crop insecticide/nematicide fungicide treated area	grass - -	carrot carbofuran Fubol	parsnip carbofuran -	turnip chlorfenvinphos -	carrot carbofuran Fubol	 100
Newlands 27-9-90 loamy sand 7.4	crop insecticide/nematicide fungicide treated area	grass - -	rye - -	rye - -	carrot carbofuran Fubol	salad onion - -	 85
Nile Road 27-9-90 loamy sand 7.3	crop insecticide/nematicide fungicide treated area	grass - -	barley - -	carrot carbofuran Fubol	barley - -	carrot carbofuran Fubol	 72
Larks Heath 27-9-90 loamy sand 7.3	crop insecticide/nematicide fungicide treated area	lucerne - -	barley - -	carrot carbofuran Fubol	turnip carbosulfan -	parsnip carbofuran -	 24
Beccles 15-10-90 loamy peat 6.1	crop insecticide/nematicide fungicide treated area untreated area		wheat - -	linseed - -	beans - -	sugar beet carbosulfan -	 38 23
PW 122 8-11-90 loamy sand 7.4	crop insecticide/nematicide fungicide treated area untreated area	carrot carbofuran -	beans - -	turf - -	turf - -	beans - -	 35 12
PW 123 8-11-90 loamy sand 7.3	crop insecticide/nematicide fungicide treated area untreated area		carrot carbofuran Fubol	potato aldicarb Patafol x 7	beans - -	barley - -	 32 15
Dunwich 8-11-90 loamy sand 6.9	crop insecticide/nematicide fungicide treated area untreated area		barley - -	carrot carbofuran Fubol	barley - -	barley - -	 10 10

Fubol = mancozeb + metalaxyl
Patafol Plus = manganese zinc ethylenebisdithiocarbamate + oforace

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Table 2: Phorate study. Phorate treatment histories, soil properties and persistence of total phorate residues in 32 soils

No.	SOIL SITE	PHORATE TREATMENT HISTORY	ORGANIC MATTER %	pH	H_2O @ 33KPa (%)	WEEKS FOR 50% LOSS	WEEKS FOR 90% LOSS
1	Norfolk	Treated 1983 & 1990	48.2	7.6	44.9	1	3
1A	"	No previous treatment	25.6	7.8	27.3	9	> 12
2	"	Treated 1986, 1989 & 1990	57.7	7.4	47.4	1	5
2A	"	No previous treatment	49.2	7.7	40.7	11	> 12
3	"	Treated 1982 & 1989	36.0	7.5	35.2	5	> 12
3A	"	No previous treatment	25.9	7.9	28.8	10	> 12
4	"	Treated 1984 & 1988	60.0	7.5	46.7	6	> 12
4A	"	No previous treatment	41.4	8.1	34.2	10	> 12
5	"	Treated 1980 & 1987	72.9	6.3	53.4	> 12	> 12
5A	"	No previous treatment	59.5	7.3	45.7	11	> 12
6	Cambs	1990 only, nil for > 20 yr	29.5	6.6	28.7	> 16	> 16
7	"	1990 only, nil for > 20 yr	41.3	6.5	35.6	> 16	> 16
8	"	1990 only, nil for > 20 yr	44.7	6.9	33.2	> 16	> 16
9	"	1990 only, nil for > 20 yr	46.7	6.6	35.0	> 16	> 16
10	"	1990 only, nil for > 20 yr	43.7	6.4	35.7	> 16	> 16
11	"	1990 only, nil for > 20 yr	4.3	8.4	16.5	2	6
12	"	1990 only, nil for > 20 yr	4.4	8.3	17.3	4	13
13	"	1990 only, nil for > 20 yr	4.4	8.3	17.8	2	9
14	"	1984, 1990	19.1	7.4	23.6	10	> 20
15	"	1984, 1990	26.4	6.9	28.9	5	> 16
16	"	1990 only, nil for > 12 yr	26.6	7.8	37.1	3	7
17	Norfolk	1984, 1990	49.0	7.6	42.8	4	14
18	"	1984, 1990	36.6	7.6	32.6	3	> 14
19	"	1978, 1984, 1990	65.8	7.4	48.2	5	> 14
20	"	1978, 1984, 1990	57.9	7.4	47.5	1.5	4
21	Suffolk	Treated 1989 & 1990	14.1	7.8	19.1	1.5	3
22	"	Treated 4 yr out of last 10 yr	13.7	6.8	16.1	7	> 16
23	"	Treated 1984 - 1987	4.7	8.5	27.8	3	6
24	"	Treated 3 yr out of last 10 yr	4.4	8.2	23.9	2	4
25	"	Treated 3 yr out of last 6 yr	5.7	8.1	25.5	1.5	3
26	"	Treated 3 yr out of last 10 yr	5.3	8.0	26.5	4	7
27	"	No previous treatment	7.5	8.0	28.2	4	11

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Table 3: Associations between the stability of freshly applied phorate in previously-treated and previously-untreated soils and a) soil pH and b) soil organic matter content

a) Soil pH

Numbers of previously-treated soils

pH	Initial half-life < 4 weeks	Initial half-life > 4 weeks
> 7.4	14	4
< 7.4	0	8

Numbers of previously-untreated soils

pH	Initial half-life < 4 weeks	Initial half-life > 4 weeks
> 7.4	1	4
< 7.4	0	1

b) organic matter

Numbers of previously-treated soils

organic matter %	Initial half-life < 4 weeks	Initial half-life > 4 weeks
< 10	7	0
> 10	7	12

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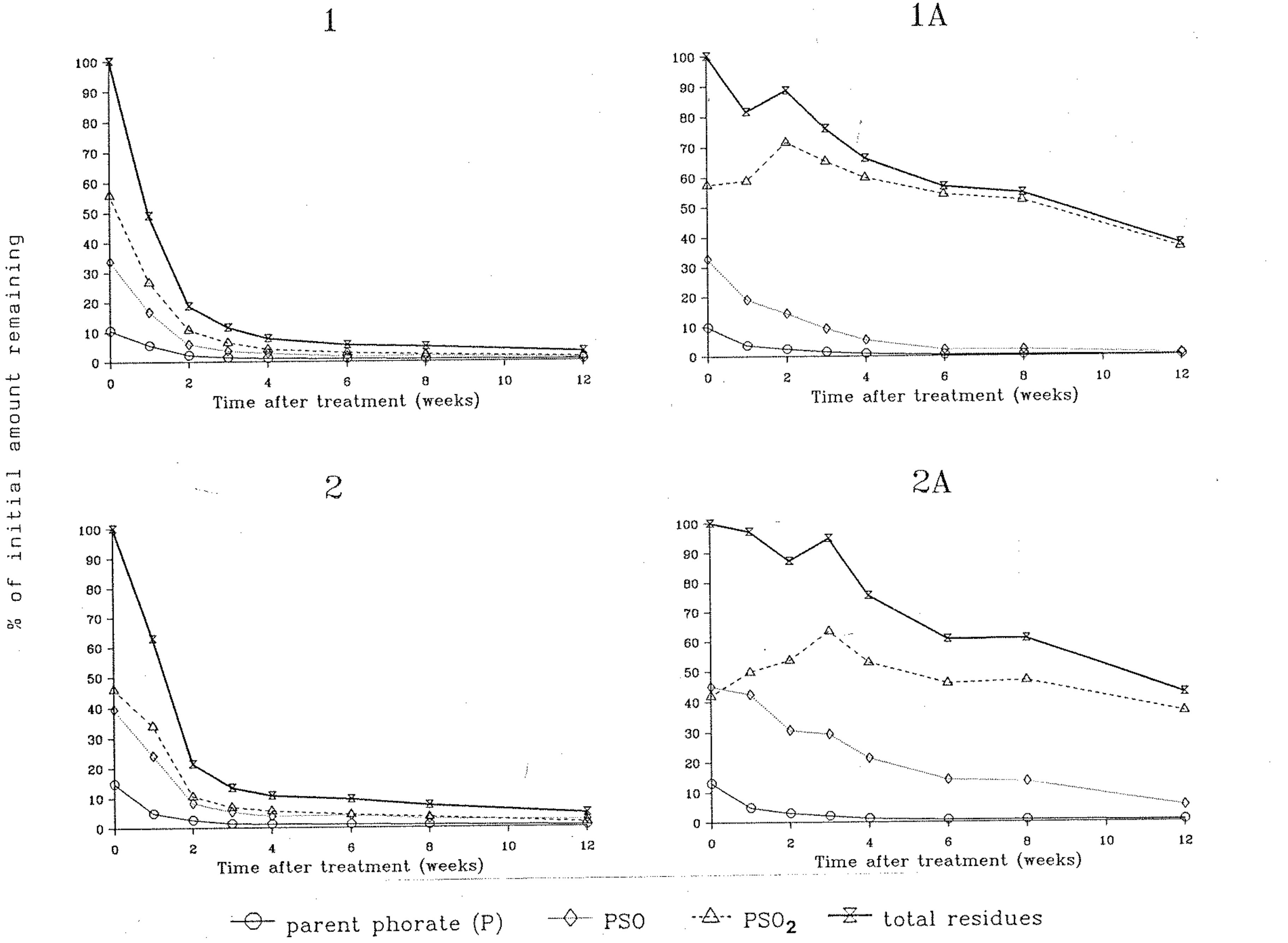
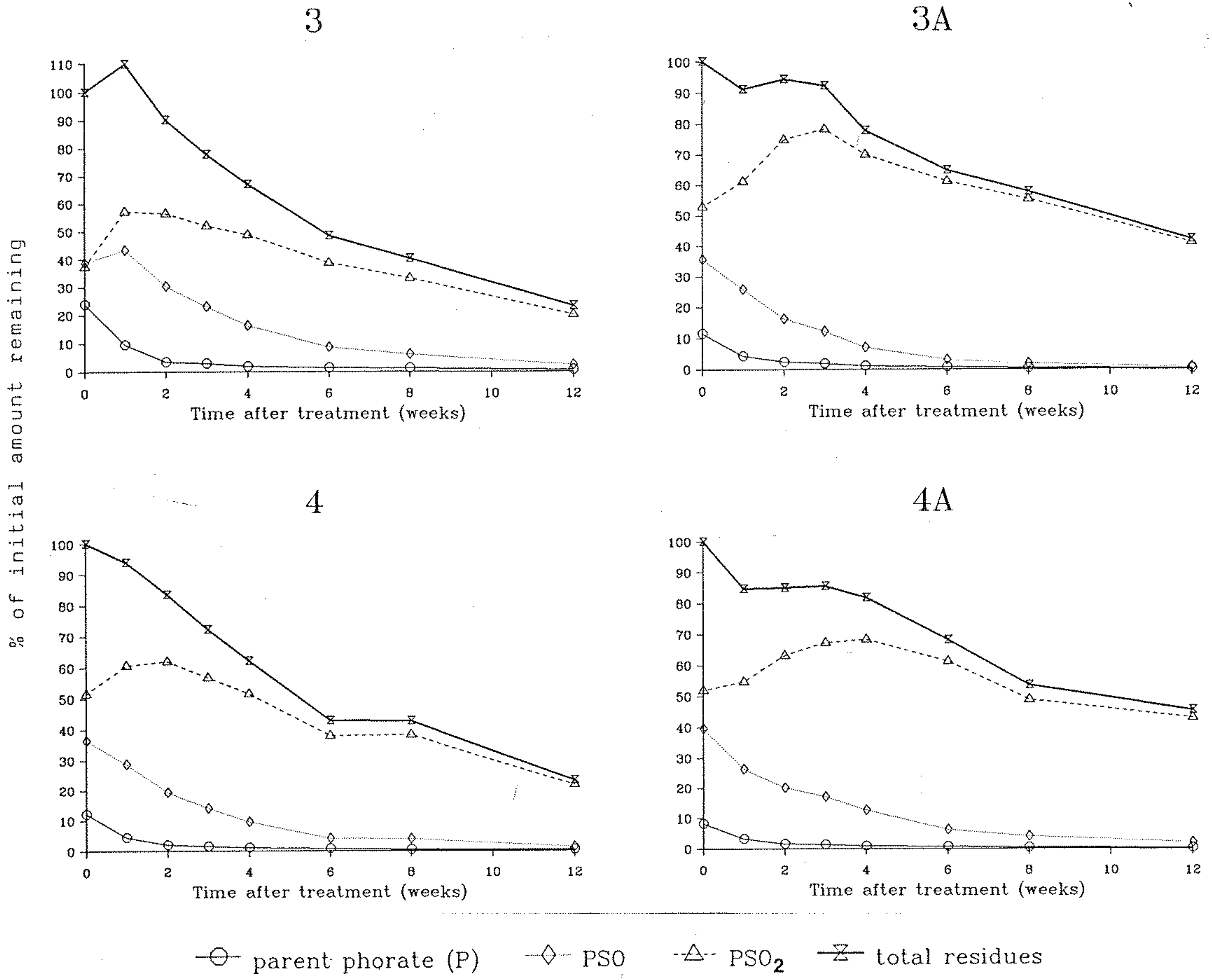
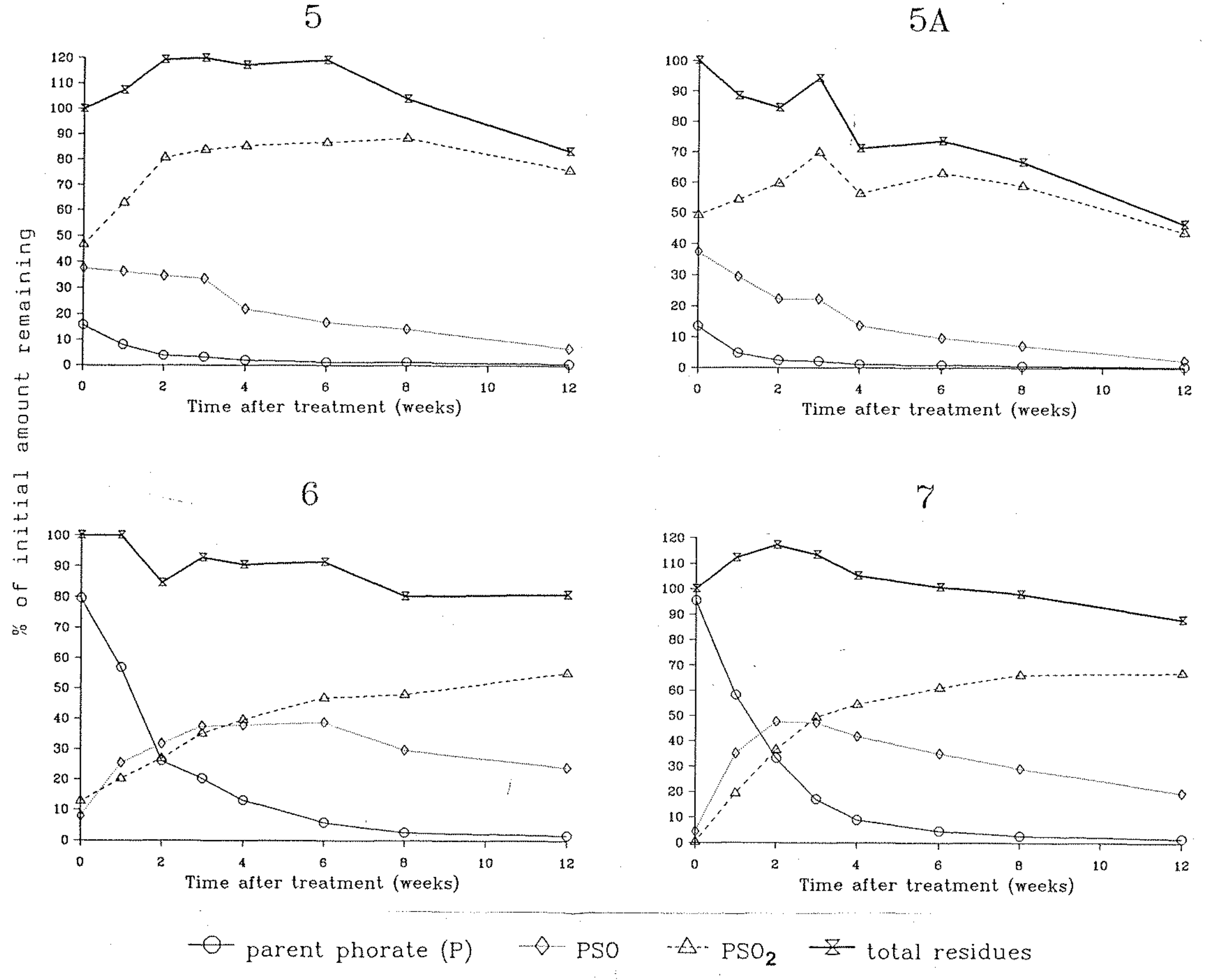
Degradation of freshly-applied phorate in soils 1-27



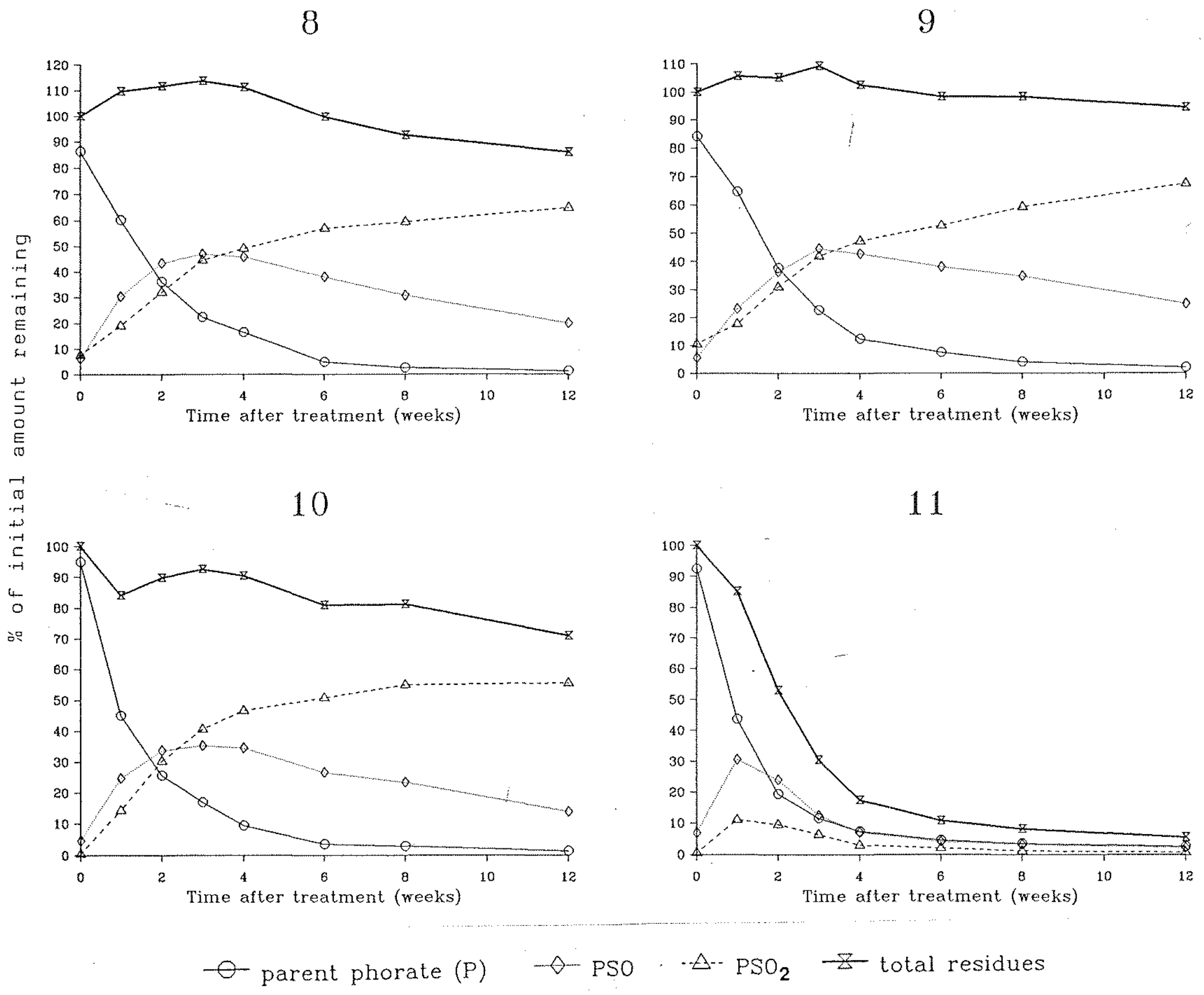
Degradation of freshly-applied phorate in soils 1-27



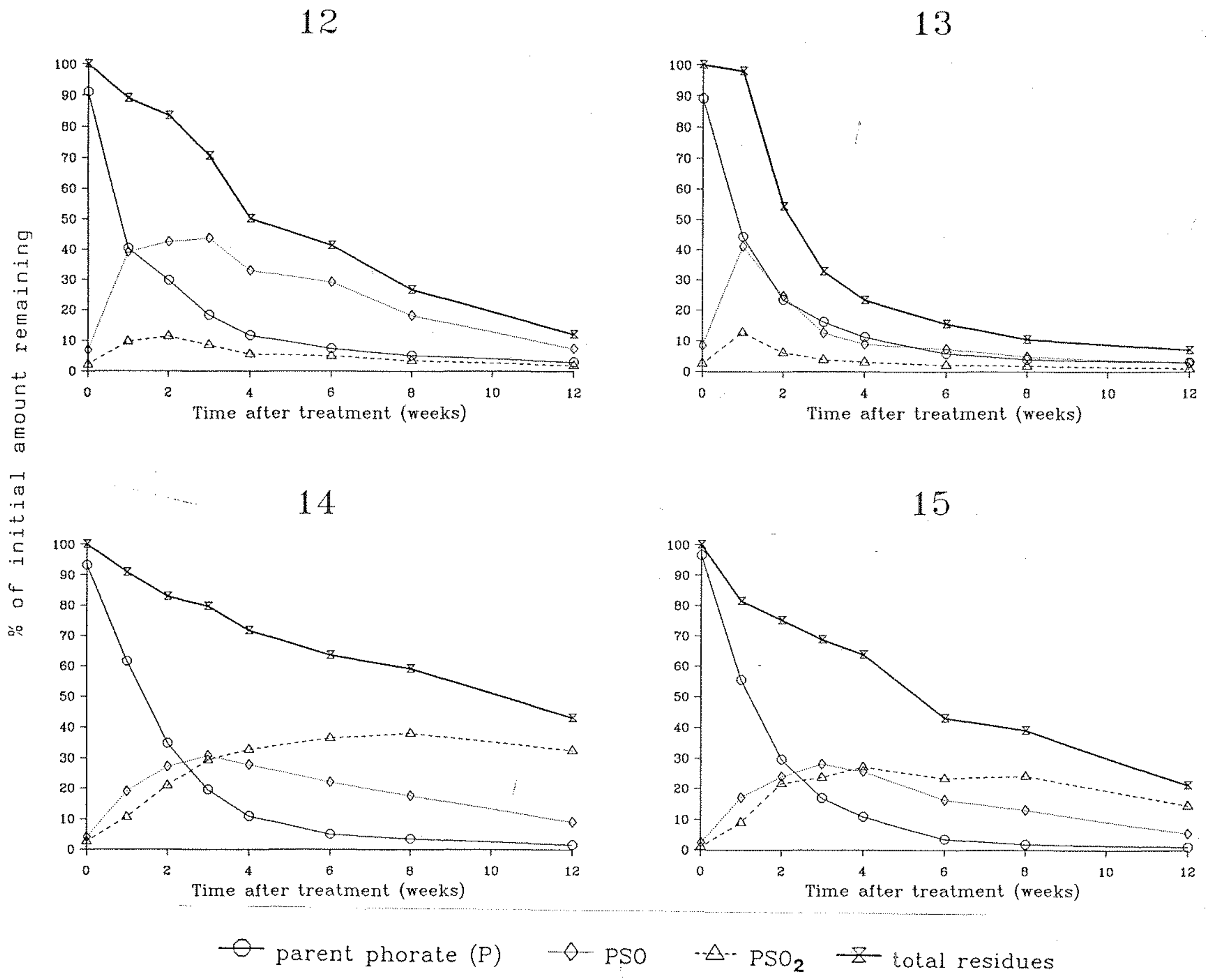
Degradation of freshly-applied phorate in soils 1-27



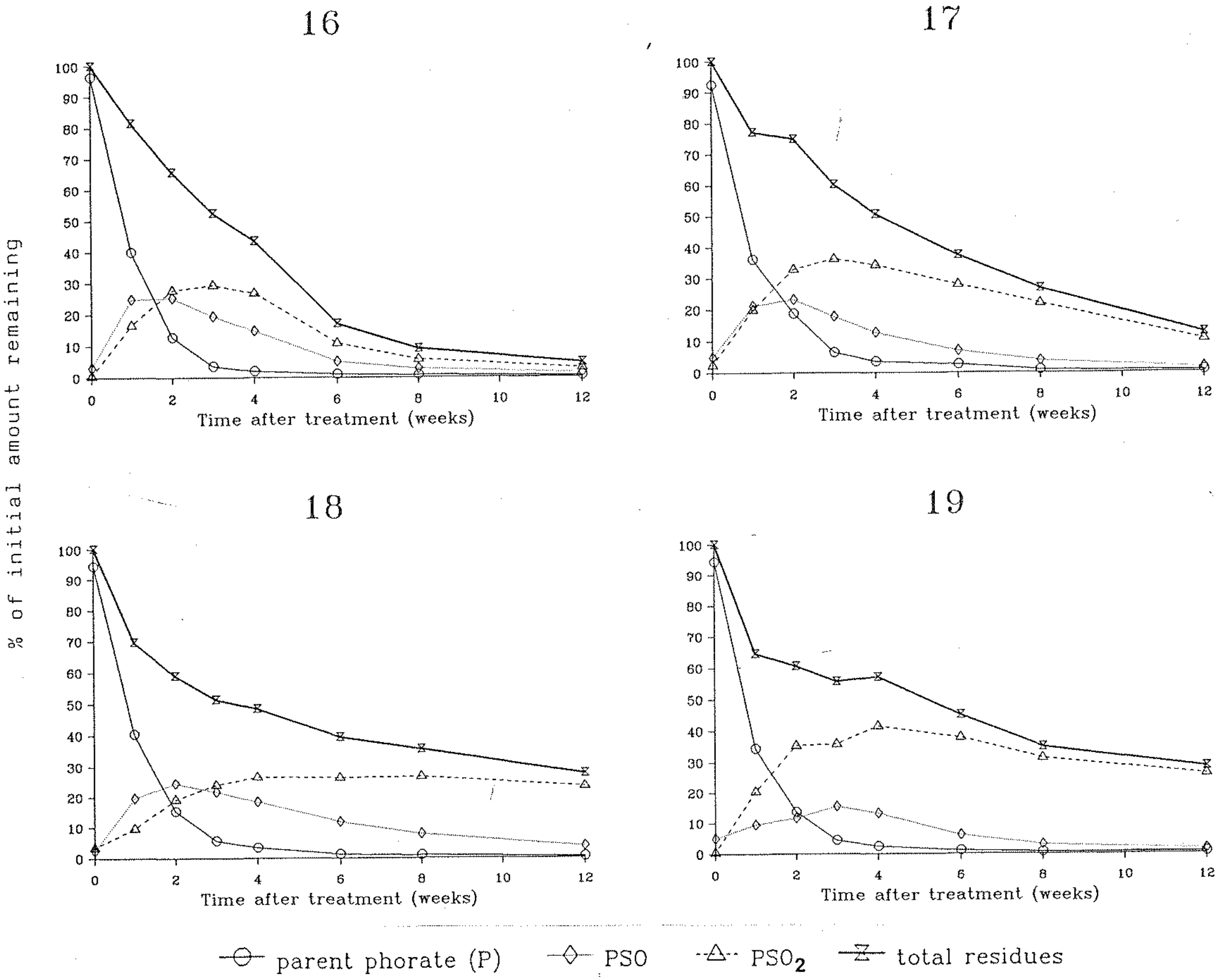
Degradation of freshly-applied phorate in soils 1-27



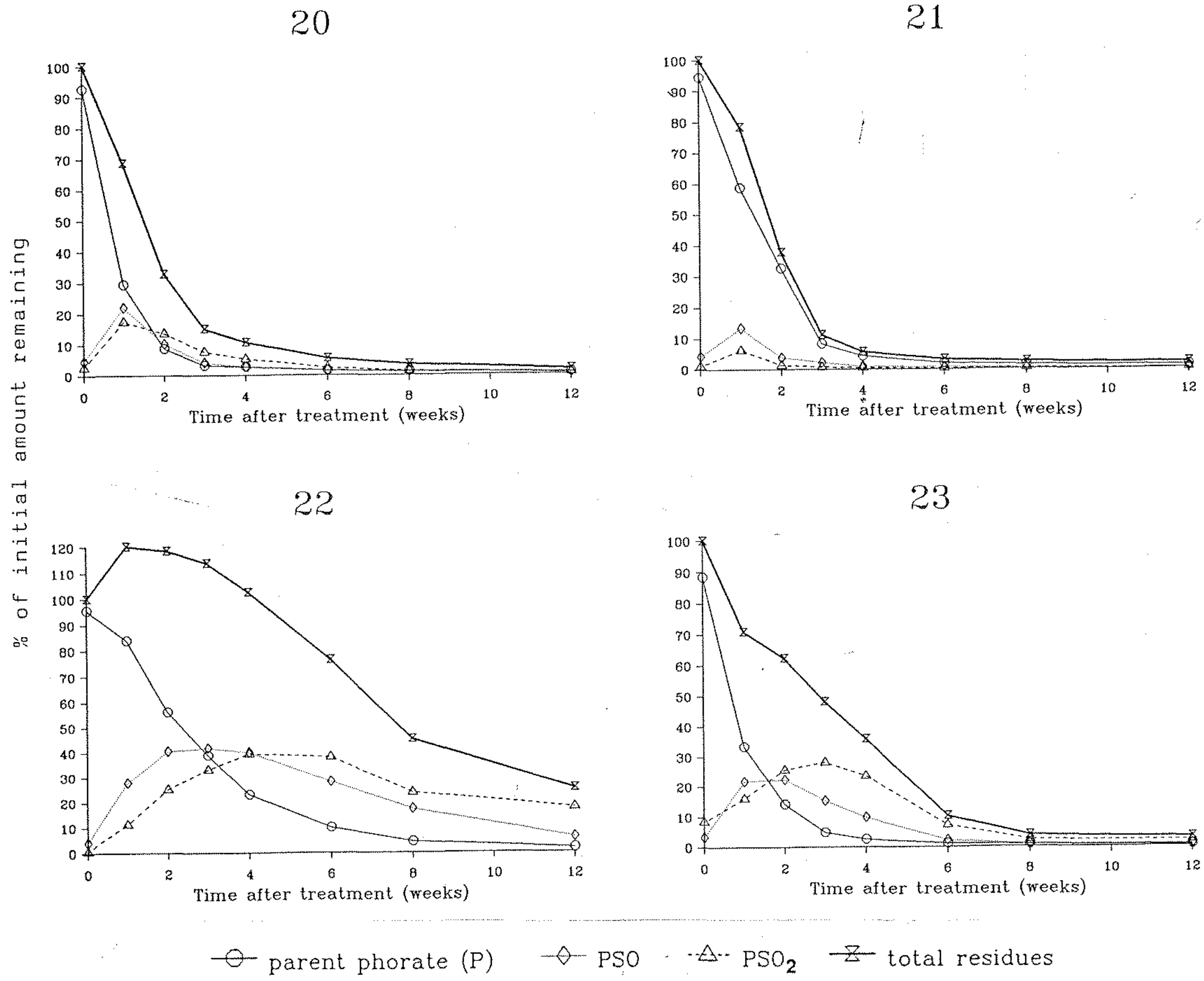
Degradation of freshly-applied phorate in soils 1-27



Degradation of freshly-applied phorate in soils 1-27



Degradation of freshly-applied phorate in soils 1-27



Degradation of freshly-applied phorate in soils 1-27