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PRESERVATION OF ORGANICS. PART I. STABILITY OF ORGANOCHLORINATED INSECTICIDES IN PRESERVED NATURAL WATER SAMPLES

by

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PERSPECTIVE-GESTION

Depuis la centralisation des laboratoires d'analyse de la qualité de l'eau à l'échelle du Canada, des échantillons provenant des régions du Pacifique et du Yukon, de l'Ouest et du Nord, du Québec, de l'Atlantique et de l'Ontario sont envoyés au Laboratoire national de la qualité des eaux, à Burlington, pour y être analysés. Il arrive souvent que les échantillons doivent être entreposés un certain temps avant que les données puissent être extraites et analysées. Pour tirer des résultats valables de ces échantillons, il faut donc veiller à ce qu'ils ne subissent aucune détérioration entre l'étape de leur prélèvement et celle de leur analyse. Dans de nombreux cas, on ne connaît que très peu ou même pas du tout la stabilité des paramètres organiques dans les échantillons d'eau et de sédiments. Il devenait donc nécessaire de procéder à une série d'études en vue de mettre au point des techniques pour la conservation de substances organiques dans des échantillons naturels faisant l'objet d'analyses courantes.

La présente étude avait pour objet d'évaluer les techniques de conservation d'insecticides organochlorurés courants dans des échantillons d'eau naturelle. On a aussi vérifié l'efficacité de la technique de conservation choisie en déterminant en laboratoire la stabilité des insecticides dans des échantillons d'eau provenant de cinq régions. À l'exception de l'endrine, tous les insecticides se sont révélés stables pendant au moins 10 à 15 semaines.

RÉSUMÉ

L'étude visait à déterminer la stabilité de 19 insecticides organochlorurés courants ajoutés à des échantillons d'eau provenant de cinq régions. L'étude s'est déroulée en deux étapes distinctes. On a tout d'abord procédé à une étude pilote ayant pour objet d'évaluer l'efficacité de deux agents de conservation (le sulfate de cuivre et le chloroforme) pouvant être utilisés pour lesdits insecticides. L'étude pilote, faite à partir d'eau du lac Ontario, a révélé que le chloroforme était plus efficace que le sulfate de cuivre pour conserver les insecticides organochlorurés dans l'eau. Pour l'étude proprement dite, des échantillons d'eau subdivisés ont été additionnés d'insecticides, conservés dans du chloroforme et entreposés dans l'obscurité à 4 °C. Pour évaluer la stabilité des insecticides dans l'eau, on a analysé les échantillons au point de départ, puis après 3, 6, 10 et 15 semaines d'entreposage. Les résultats de l'étude ont démontré qu'à quelques exceptions près, les insecticides ont été stables pendant les quinze semaines qu'a duré l'étude. On n'a cependant pu déterminer la stabilité de l'endrine dans les échantillons d'eau en raison de la fluctuation des résultats.

MANAGEMENT PERSPECTIVE

Since the occurrence of centralization of Water Quality Laboratories across Canada, test samples are being shipped from the Pacific and Yukon, Westernand Northern , Quebec, Atlantic and Ontario regions to the Water Quality National Laboratory in Burlington for analysis. Frequently, samples will have to be stored for a period of time before extraction and analysis can be performed. In order to obtain meaningful results for the samples, their integrity must be maintained from the time of collection until the time of analysis. In many instances, the information regarding the stability of organic parameters in water and sediment samples is lacking or incomplete. A series of studies was thus required to develop techniques for the preservation of the routinely analyzed organics in natural samples.

The present study evaluated the techniques to preserve the common organochlorinated insecticides (OCs) in natural water samples. Further validation of the chosen preservation technique was provided by monitoring the stability of OCs in five regional water samples under laboratory controlled conditions. Except for endrin, all OCs in the preserved water samples were stable for at least 10 to 15 weeks.

ABSTRACT

This study monitored the stability of 19 common organochlorinated insecticides (OCs) in fortified water samples from five regions. The study was implemented in two parts. A pilot study was designed to evaluate the efficacy of two potential preservatives, i.e. copper sulfate and chloroform, for OCs. Using Lake Ontario water as a typical sample, results in the pilot study indicated that chloroform was a more effective preservative than copper sulfate for OCs in water. In the full scale study, subsamples of the five regional waters were fortified, preserved with chloroform, and stored at 4°C in the dark. The stability of OCs in the waters was monitored by analyzing the samples at 0-time, as well as after 3, 6, 10 and 15 weeks of storage. Results in the full scale study showed that, except for a few cases, the OCs in the preserved water samples were stable over the 15-week study period. The stability of endrin in these water samples was unknown because of erratic recoveries.

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INTRODUCTION

Since the occurrence of centralization of Water Quality Laboratories across Canada, test samples are being shipped from the Pacific and Yukon, Western and Northern, Quebec, Atlantic and Ontario regions to the Water Quality National Laboratory (WQNL), Burlington, for analysis. Compared to most trace metals and major ions, organics and pesticides are usually less stable in environmental matrices. Also, organic analytical procedures are frequently lengthly so that it is impractical for a laboratory to analyze the samples as soon as they arrive. This implies that samples will have to be stored for a period of time until extraction and analysis can be performed. In order to obtain meaningful results, the integrity of samples must be maintained from the time of collection until they are analyzed.

Organochlorinated insecticides (OCs) in water are frequently analyzed by the WQNL. Therefore, the first task of this preservation study was to determine the stability of OCs in preserved water samples. Although there were a few reports on this subject in the literature (1, 2), the studies were carried out under conditions irrelevant to our objectives. In this work, we developed a technique to preserve OCs in water and monitored the stability of the insecticides over a period of up to 15 weeks under controlled conditions.

STUDY DESIGN

The 19 OCs included in this study are listed in Table 1. The sources of the five regional water samples used in this study are given in Table 2. For simplicity, the province of origin (e.g. British Columbia, New Brunswick, Ontario, Quebec, Saskatchewan) instead of the exact location where the sample was collected was used to identify each water in this report. Because of limitation in resources, only one type of water from each region and one concentration level of OCs was tested. The OC concentrations in the preserved water samples (Table 1) were higher than the levels found in most open lake surface waters. In this case, the results of test samples are more indicative of the stability of the OCs rather than analytical uncertainties if the study were carried out at levels near the detection limit. Preliminary analysis of the unspiked waters indicated that all of them had less than 5% of the spiking level of OCs in the sample blanks. Therefore, no correction was required for the calculation of recoveries.

The preservation of OCs in water was investigated in two parts:

(a) a pilot study to examine the efficacy of several preservatives, and

(b) a full scale study to monitor the stability of the 19 OCs in the above five waters using the most effective preservative determined in the pilot study over a period of up to 15 weeks.

In the pilot study, 30 one L samples of Lake Ontario water were prepared and fortified. One set of 15 samples was preserved with 2 g of $CuSO_4$, the other 15 with 10 mL chloroform. Three samples from each set were immediately analyzed to generate 0-time results. The remaining samples were kept at 4°C in the dark and analyzed in triplicate aftr 3, 6, 9 and 15 weeks of storage.

Based on the results in the pilot study, a full scale study using chloroform was set up to monitor the same OCs in the five, fortified regional waters. Samples were again stored at 4°C in the dark and four replicates of each water were analyzed after 3, 6, 10 and 15 weeks of storage. Another set of 0-time was analyzed immediately after fortification.

EXPERIMENTAL

Standard Solutions

A spiking solution in acetone was prepared for the mixture of 19 OCs according to the concentrations listed in Table 1. A GC calibration standard was prepared by making a 1:100 dilution of the spiking solution with isooctane.

Subsampling, Fortification and Preservation

Bulk water samples from the five regions were mechanically stirred in their original 100 L containers and subsampled into 1 L whiskey bottles. Each bottle was then spiked with 100 µL of the spiking solution using a syringe, followed by the addition of 10 mL of chloroform. Each bottle was then sealed with Teflon tape and screw cap. Samples were then stirred for 10 min and kept at 4°C in the dark until analysis.

Extraction and Cleanup

After the storage time had elapsed, each 1 L water sample was extracted three times with dichloromethane. The combined organic extracts were then dried through anhydrous sodium sulfate and concentrated to 3 mL by rotary evaporation. Cleanup of sample extracts was performed in a 5 g activated Florisil column. Two 50 mL fractions, one in 20+80 dichloromethane and hexane, the other in 50+49.65+0.35 dichloromethane, hexane and acetonitrile, were collected. Each fraction was concentrated down to 3 mL and made up to a final volume of 10 mL for subsequent GC analysis.

GC Analysis

All GC analyses were done with a Hewlett-Packard model 5880A gas chromatograph equipped with a Ni^{63} electron-capture detector, a model 7671A autosampler and Level 4 terminals. A 12 m x 0.2 mm i.d. OV-1 fused silica capillary column was used. A two stage oven temperature program was used: initial temperature 70°C with a 0.5 min hold, programming rate 1, 25°C/min (from 70°C to 160°C), programming rate 2, 2°C/min (from 160°C to 220°C) and a 15 min hold at the final temperature. Temperatures for the injection port and detector were 250°C and 300°C, respectively. Carrier gas was helium with a column head pressure of 10 psi. Makeup gas was argon/methane (95+5) with a 30 mL/min flow rate. Splitless injections (valve time 0.5 min) of samples were made by an autosampler.

RESULTS AND DISCUSSION

Recovery data for the pilot preservation study of OCs in Lake Ontario water are presented in Table 3 ($CuSO_4$ preserved samples) and Table 4 (chloroform preserved samples). Recovery data for OCs in the full scale study with all five regional waters are summarized in Tables 5 through 9. Recoveries of individual OC in each water are also plotted against the storage period (Figures 1 through 19).

PILOT STUDY

Before the study began, several potential techniques were considered for the preservation of OCs in water. However, because of the known hydrolysis and dehydrochlorination of some labile OCs under acidic and basic conditions (3), the use of acids and bases were eliminated. Since copper sulfate and chloroform have been used to preserve pesticides and organics in water samples (4), their efficiency to preserve OCs in water was evaluated. Using fortified Lake Ontario water as typical samples, the recoveries of OCs at 0-time, and after 3, 6, 9 and 15 weeks of storage time were determined. For the copper sulfate preserved samples, the results (Table 3) clearly indicated that the recoveries of HCB, heptachlor, aldrin, pp'-DDE, op'-DDT, and pp'-DDT were continuously decreasing throughout the 15-week study period. On the other hand, all the OCs in the chloroform preserved samples were consistently recovered over the same study period. On this basis, chloroform was selected as an effective preservative for OCs in water and its efficiency was further validated with the other regional waters in the following full scale study.

FULL SCALE STUDY

General Comments

Careful examination of the results summarized in Tables 5 through 9 indicated that the recoveries of OCs from New Brunswick and Saskatchewan waters were generally lower than the other three waters. Lower recovery was likely due to the formation of emulsions in the solvent extraction step because of the presence of large amounts of humic substances and coloured materials in these two samples. It was also noted that the recoveries of HCB, α- and γ-BHC, aldrin and heptachlor were lower and less precise than the rest of the OCs in all waters. This was likely due to the volatility of such compounds and losses were experienced during the solvent evaporation steps. Another anomaly was observed for the week 3 results for which the recoveries for the 19 OCs in all samples were generally lower than those for 0-time, weeks 6, 10 and 15. Reason for the lower recoveries was unknown yet it might be due to a systematic error which was not discovered and corrected when those samples were extracted and analyzed.

Specific Comments

HCB, the BHC isomers, heptachlor and aldrin

The recovery of HCB was the lowest among the 19 OC's and it ranged from 50 to 65% throughout the entire study period, including 0-time. Low recovery of HCB was consistent with its volatility, level of spike and the analytical methodology used. Recoveries of α-BHC, γ-BHC, heptachlor and aldrin ranged from 60 to 75% in all five regional waters. Again these recoveries were lower than the other OCs since they are also relatively volatile. The recovery of β-BHC was the highest in this group and it ranged from 80 to 90% over the study period. It should be noted that, even though heptachlor was reported to be hydrolyzed in water under environmental conditions, the use of chloroform and storage at 4°C in the dark effectively prevented the degradation of this OC for at least 15 weeks.

Heptachlor epoxide, α- and γ-chlordane

Recoveries of these three OCs from the fortified water samples were close to quantitative. Except for the week 15 samples for BC and Quebec of which the heptachlor epoxide recovery was slightly above 100%, the recoveries of these three OC's were consistently between 85 and 95% in all other samples.

The DDT group compounds

Similar to the previous group, pp'-DDE and pp'-DDD were consistently and quantitatively recovered in all water samples over the entire study period. Recoveries of these two OCs ranged from 85 to 100%. The recoveries for op'-DDT, pp'-DDT and pp'-methoxychlor were also 85% in most cases, however, interference was experienced in some of the week 15 samples so that the apparent recoveries were over 130%. This problem was particularly severe for pp-'methoxychlor since its ECD sensitivity is low.

Endosulfans, endrin, dieldrin and mirex

In nearly all fortified water samples, the endosulfans, dieldrin and mirex were 80 to 100% recovered. Possibly due to some random interference of coextractives, recovery for dieldrin was 128% in BC water at week 15. Recovery of endrin, however, was erratic (from 46 to 99%) and interference was observed for some of the week 15 samples such that the apparent recovery was over 150%. Decomposition or adsorption of endrin due to active sites in the injection port or column or on-column reaction with sample coextractives were possible causes for erratic endrin results.

CONCLUSION

The results presented in the Tables and Figures for the OCs can be summarized below:

(1) Although there were random fluctuations in the recoveries of the insecticides over the study period, there was never a case in the chloroform preserved samples that a compound showed a continuous, i.e. 3 or 4 consecutive, decrease in recovery. The fluctuation was therefore attributed to analytical errors rather than to the instability of insecticides in the samples.

(2) Because of their volatility, some of the OCs were not quantitatively (i.e. >90%) recovered. Therefore, relative rather than absolute recoveries should be used as a basis for the determination of stability. Using the 0-time recovery as a reference, the relative recoveries (week x over 0-time) of all OCs never fell below 75% of their 0-time values.

(3) Based on the finding of 1 and 2 above, it is concluded that, with the following exceptions, the OCs in regional waters are stable over the 15-week study period if the samples were preserved with

chloroform and stored at 4°C in the dark as described earlier. Because of interference in some week 15 samples, the stability of op'-DDT, pp'-DDT, pp'-methoxychlor, and dieldrin in the British Columbia and New Brunswick waters could not be ascertained, although the same compounds were stable in the other waters. Nevertheless, the above four compounds in the preserved water samples were stable for at least ten weeks. Because of erratic recoveries, the stability of endrin in these water samples could not be confirmed.

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Table 1 List of the 19 Organochlorinated Insecticides and Their Concentrations Used in the Preservation Study.

Parameter	Concentration of OC in Water (µg/L)	Concentration of OC in Spiking Solution (µg/mL)
α-BHC	0.1	1
β-BHC	0.1	1
γ-BHC	0.1	1
HCB	0.1	1
Heptachlor	0.1	1
Aldrin	0.1	1
Heptachlor epoxide	0.1	1
γ-Chlordane	0.1	1
α-Endosulfan	0.2	2
α-Chlordane	0.1	1
Dieldrin	0.2	2
pp'-DDE	0.2	2
Endrin	0.4	4
pp'-DDD	0.4	4
β-Endosulfan	0.2	2
op'-DDT	0.4	4
pp'-DDT	0.4	4
pp'-Methoxychlor	0.4	4
Mirex	0.2	2

Table 2. List of Natural Water Samples Used in the Preservation Study for OCs.

Region	Site
Atlantic	Mersey River at Jakes Landing, N.S.
Ontario	Station 23, Lake Ontario
Pacific	Fraser River, B.C.
Quebec	R. Outauais, NAQUADAT Station 05QU022LV9001
Western	East Proper River, Saskatchewan, NAQUADAT Station 00SA11AE008

Table 3. Mean Recovery of OCs in Copper Sulfate Preserved Lake Ontario water - Pilot Study (replicate of three analyses).

Pesticide	Week 0	Week 3	Week 6	Week 9	Week 15
Aldrin	78	69	56	46	41
α-BHC	91	99	86	84	85
α-Chlordane	88	79	75	71	75
α-Endosulfan	81	86	103	83	82
β-BHC	98	104	99	96	104
β-Endosulfan	88	91	102	92	91
Dieldrin	83	81	100	91	94
Endrin	83	99	89	88	85
γ-BHC	96	90	92	92	88
γ-Chlordane	95	97	74	69	70
HCB	87	82	62	60	49
Heptachlor	81	62	45	33	21
Heptachlor epoxide	82	87	96	84	90
Methoxychlor	90	109	92	96	102
Mirex	88	79	59	57	51
op'-DDT	85	91	69	57	58
pp'-DDD	90	93	70	68	79
pp'-DDE	93	89	65	59	62
pp'-DDT	84	95	80	59	66

Table 4. Mean Recovery of OCs in Chloroform Preserved Lake Ontario water - Pilot Study (replicate of three analyses).

Pesticide	Week 0	Week 3	Week 6	Week 9	Week 15
Aldrin	78	82	70	76	83
α-BHC	84	77	65	79	68
α-Chlordane	84	96	78	89	97
α-Endosulfan	89	88	98	98	89
β-BHC	88	101	78	89	105
β-Endosulfan	91	90	101	104	87
Dieldrin	84	94	104	104	97
Endrin	88	89	101	98	100
γ-BHC	95	91	70	96	90
γ-Chlordane	87	96	77	85	96
HCB	72	61	62	66	50
Heptachlor	78	78	72	73	77
Heptachlor epoxide	84	98	93	97	95
Methoxychlor	85	87	97	95	91
Mirex	91	96	86	92	98
op'-DDT	83	99	89	92	97
pp'-DDD	87	96	80	94	95
pp'-DDE	87	94	82	89	98
pp'-DDT	85	99	93	97	97

Table 5. Mean Recovery of OCs in Fortified and Preserved British Columbia Water - Full Scale Study (replicate of four analyses).

Pesticide	Week 0	Week 3	Week 6	Week 10	Week 15
Aldrin	77	66	78	73	75
α-BHC	78	63	80	64	73
α-Chlordane	88	79	94	87	90
α-Endosulfan	89	80	90	93	102
β-BHC	81	80	98	84	98
β-Endosulfan	87	85	96	98	95
Dieldrin	89	85	93	99	128
Endrin	68	46	81	85	272
γ-BHC	79	67	83	72	71
γ-Chlordane	93	83	89	88	93
HCB	57	56	66	57	64
Heptachlor	78	63	76	66	83
Heptachlor epoxide	84	83	93	96	112
Methoxychlor	82	89	83	94	312
Mirex	99	86	95	90	98
op'-DDT	98	80	97	90	118
pp'-DDD	95	91	102	91	99
pp'-DDE	86	83	99	88	92
pp'-DDT	94	87	94	89	141

Table 6. Mean Recovery of OCs in Fortified and Preserved New Brunswick Water - Full Scale Study (replicate of four analyses).

Pesticide	Week 0	Week 3	Week 6	Week 10	Week 15
Aldrin	62	74	70	71	78
α-BHC	59	69	65	67	72
α-Chlordane	82	84	90	90	97
α-Endosulfan	85	87	89	85	98
β-BHC	91	85	100	88	104
β-Endosulfan	94	90	89	97	99
Dieldrin	82	92	91	92	112
Endrin	69	59	97	78	202
γ-BHC	62	66	75	72	74
γ-Chlordane	85	87	90	92	99
HCB	50	54	51	59	59
Heptachlor	57	67	70	67	80
Heptachlor epoxide	79	89	89	85	100
Methoxychlor	93	99	103	90	255
Mirex	88	90	91	98	102
op'-DDT	90	85	94	96	127
pp'-DDD	87	96	92	98	101
pp'-DDE	85	87	92	94	102
pp'-DDT	90	92	100	97	150

Table 7. Mean Recovery of OCs in Fortified and Preserved Lake Ontario Water - Full Scale Study (replicate of four analyses).

Pesticide	Week 0	Week 3	Week 6	Week 10	Week 15
Aldrin	73	67	73	76	76
α-BHC	73	65	67	61	70
α-Chlordane	96	84	83	83	92
α-Endosulfan	92	83	79	85	80
β-BHC	93	75	88	82	94
β-Endosulfan	92	94	89	90	88
Dieldrin	96	90	96	92	92
Endrin	91	74	80	85	90
γ-BHC	79	62	78	69	78
γ-Chlordane	98	88	84	86	94
HCB	65	51	55	53	56
Heptachlor	74	69	70	65	73
Heptachlor epoxide	92	94	83	81	89
Methoxychlor	90	82	99	95	105
Mirex	97	92	95	95	98
op'-DDT	101	93	100	91	100
pp'-DDD	91	90	93	92	101
pp'-DDE	94	98	99	87	100
pp'-DDT	92	85	90	92	97

Table 8. Mean Recovery of OCs in Fortified and Preserved Quebec Water - Full Scale Study (replicate of four analyses).

Pesticide	Week 0	Week 3	Week 6	Week 10	Week 15
Aldrin	79	67	79	61	77
α-BHC	71	71	74	56	70
α-Chlordane	90	82	97	84	90
α-Endosulfan	92	85	94	86	98
β-BHC	88	80	105	84	93
β-Endosulfan	101	99	106	93	93
Dieldrin	98	91	98	94	102
Endrin	92	66	96	99	180
γ-BHC	82	73	81	67	76
γ-Chlordane	93	85	96	86	92
HCB	63	56	63	48	59
Heptachlor	74	69	77	60	75
Heptachlor epoxide	93	87	94	86	102
Methoxychlor	87	98	131	91	107
Mirex	98	89	99	92	97
op'-DDT	99	89	101	94	103
pp'-DDD	91	91	101	92	97
pp'-DDE	91	87	98	88	95
pp'-DDT	98	91	106	98	106

Table 9. Mean Recovery of OCs in Fortified and Preserved Saskatchewan Water - Full Scale Study (replicate of four analyses).

Pesticide	Week 0	Week 3	Week 6	Week 10	Week 15
Aldrin	67	61	77	67	73
α-BHC	68	62	64	57	74
α-Chlordane	84	81	87	83	92
α-Endosulfan	88	83	81	80	77
β-BHC	84	76	93	78	97
β-Endosulfan	94	89	85	94	84
Dieldrin	91	89	88	89	91
Endrin	85	68	82	78	90
γ-BHC	74	65	76	67	78
γ-Chlordane	88	85	86	86	95
HCB	53	53	57	53	59
Heptachlor	64	70	70	62	71
Heptachlor epoxide	89	86	84	82	88
Methoxychlor	87	102	84	87	102
Mirex	100	86	91	91	94
op'-DDT	94	95	94	87	96
pp'-DDD	91	92	89	89	98
pp'-DDE	90	80	86	85	97
pp'-DDT	88	85	92	95	92

Fig. 1. Recovery of aldrin

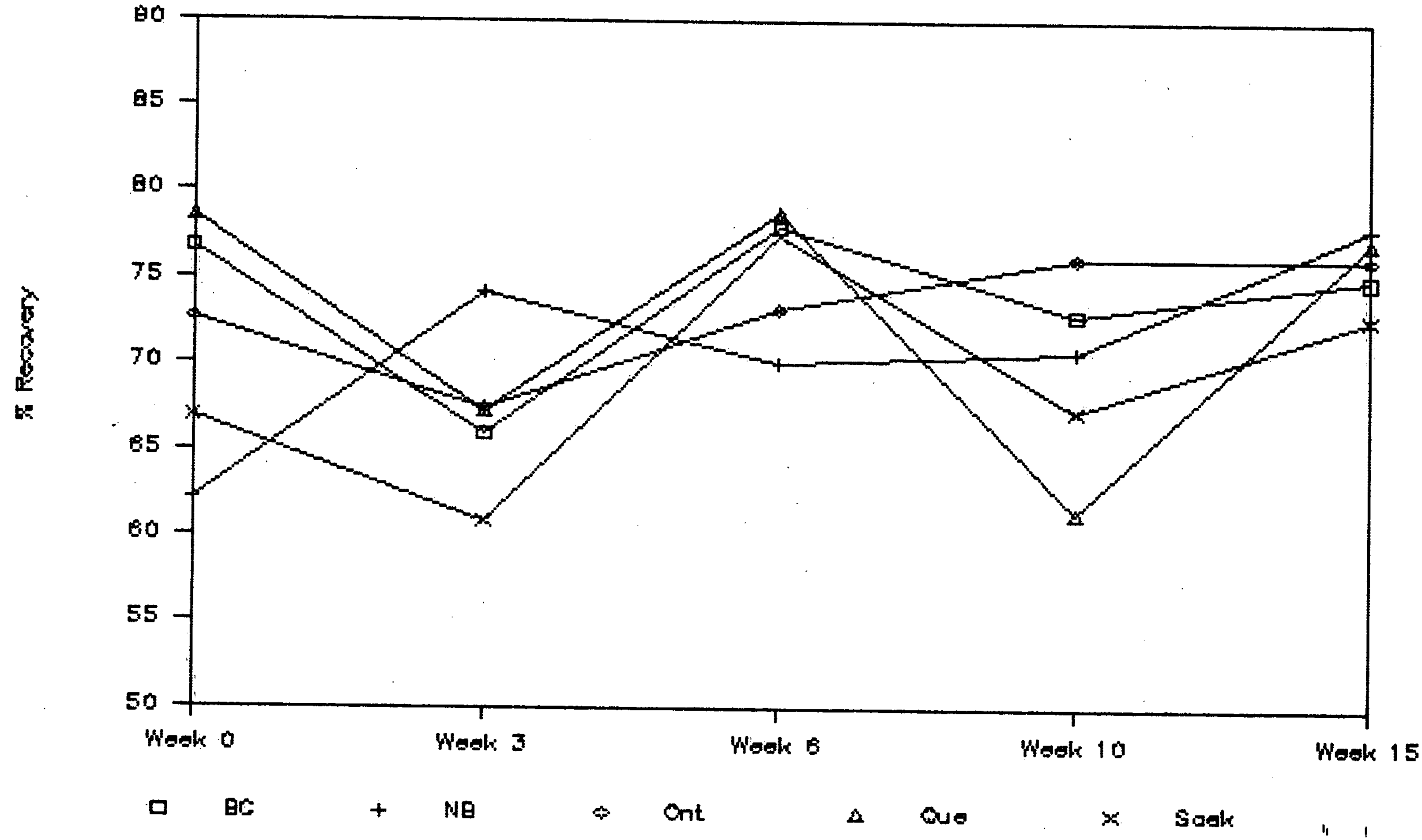

Fig. 2. Recovery of a—BHC

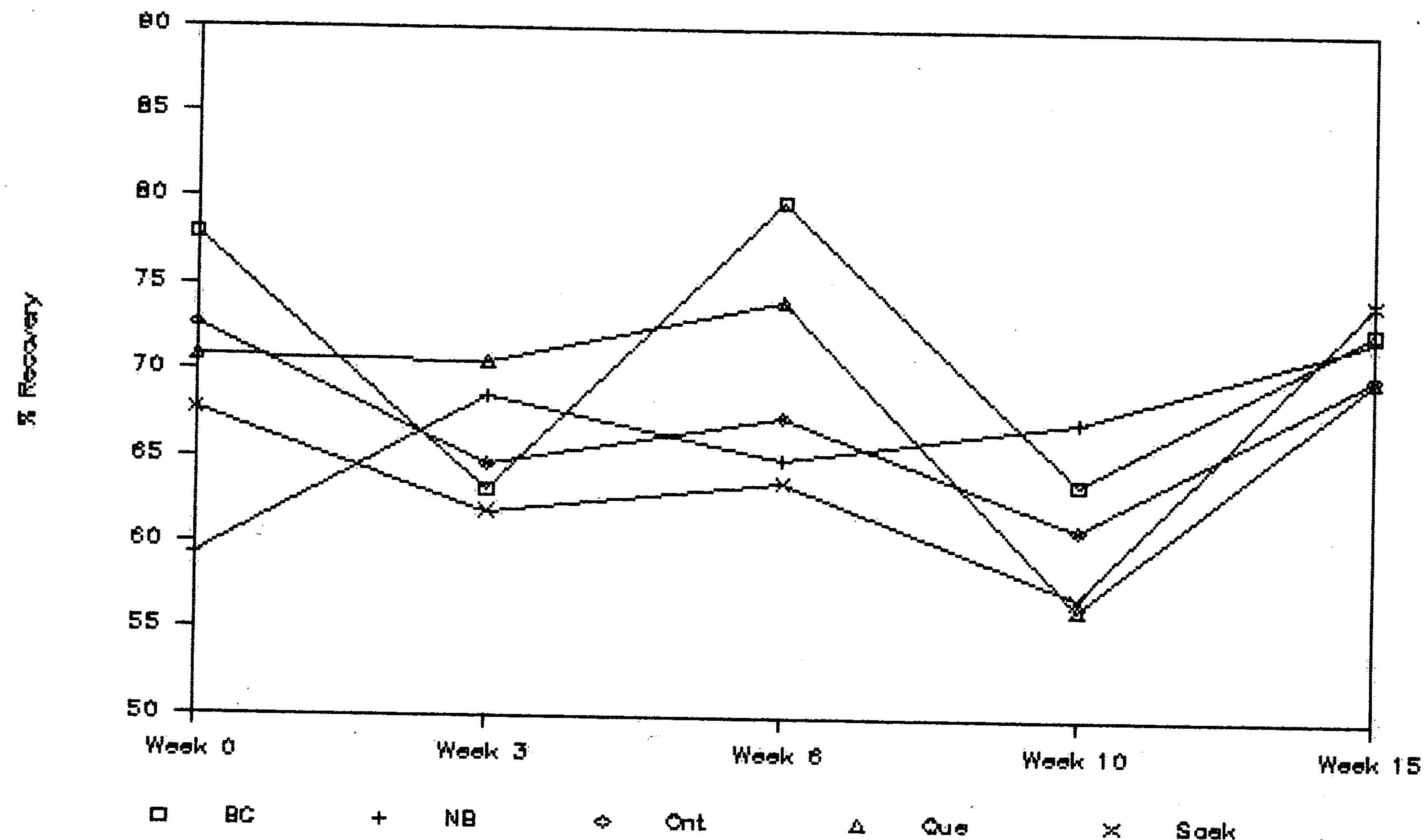

Fig. 3. Recovery of a-Chlordane

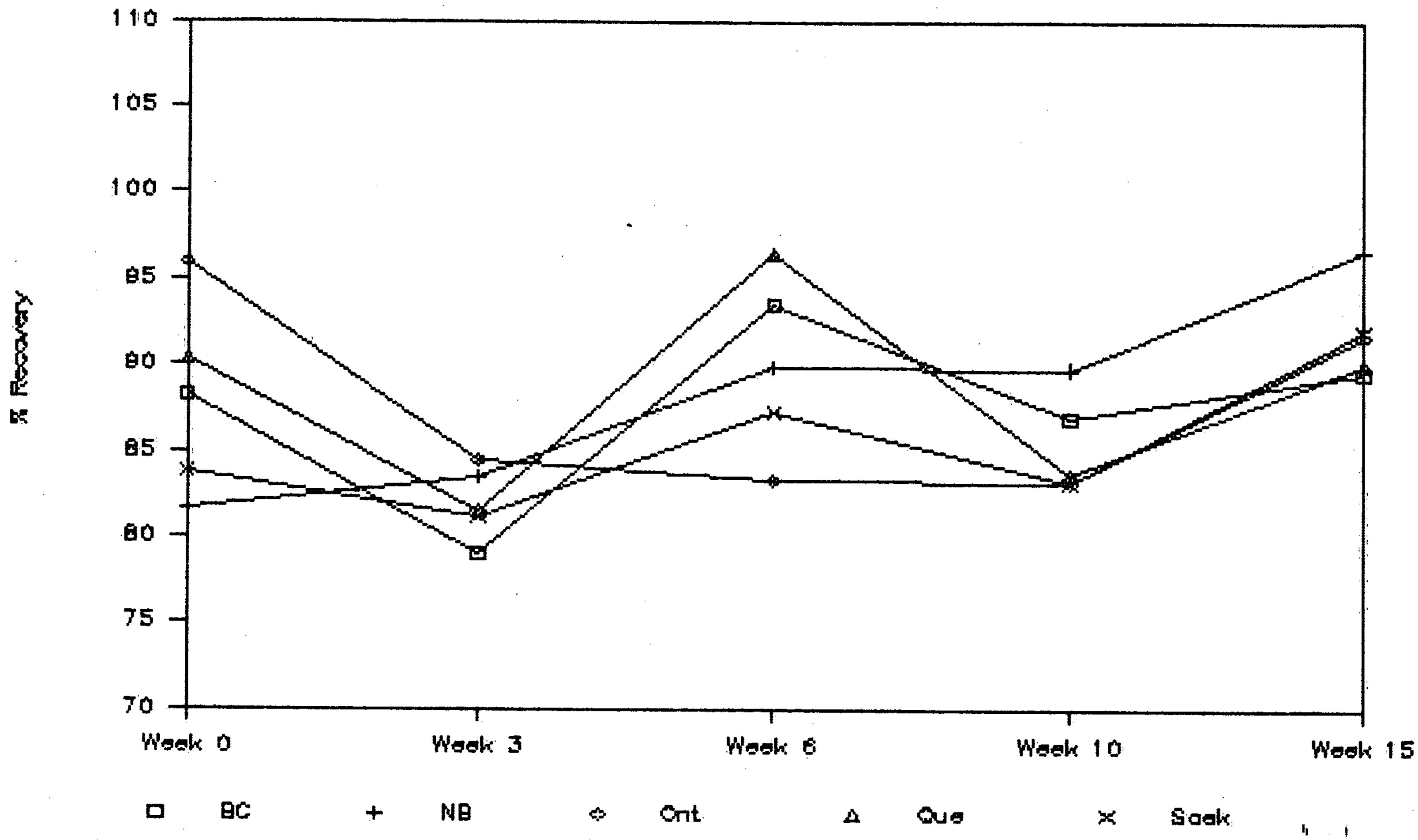

Fig. 4. Recovery of a-Endosulfan

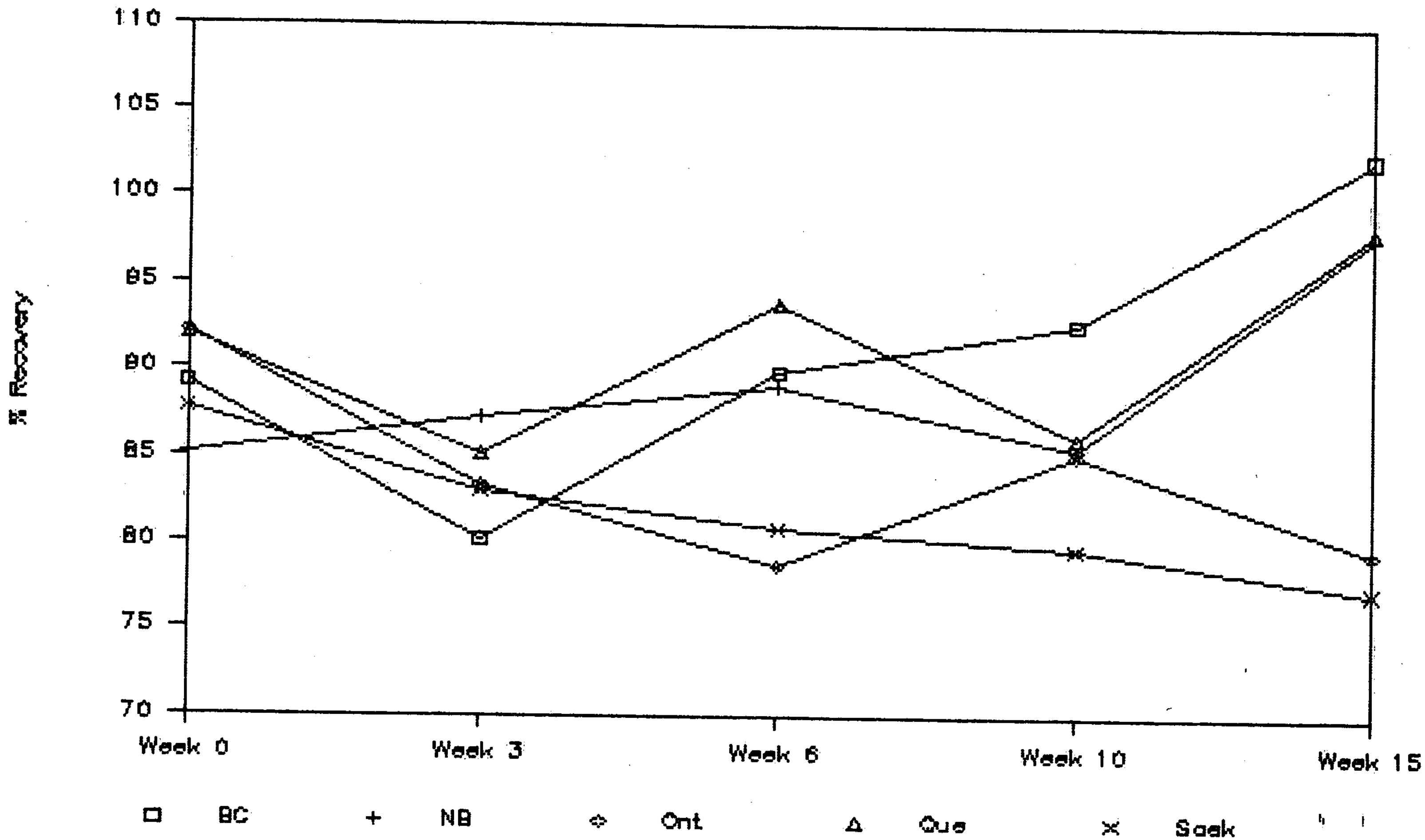

Fig. 5. Recovery of b-BHC

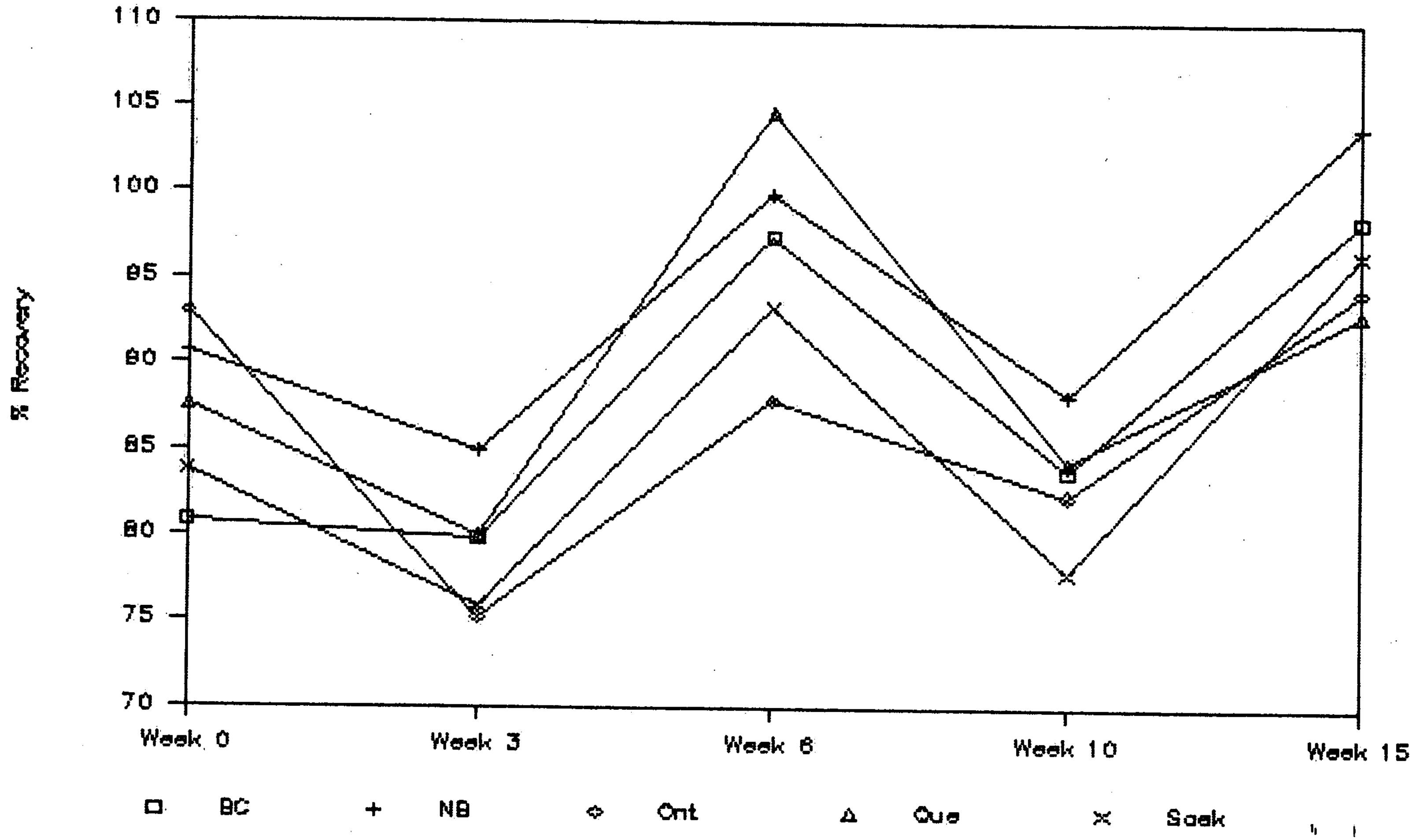

Fig. 6. Recovery of b–Endosulfan

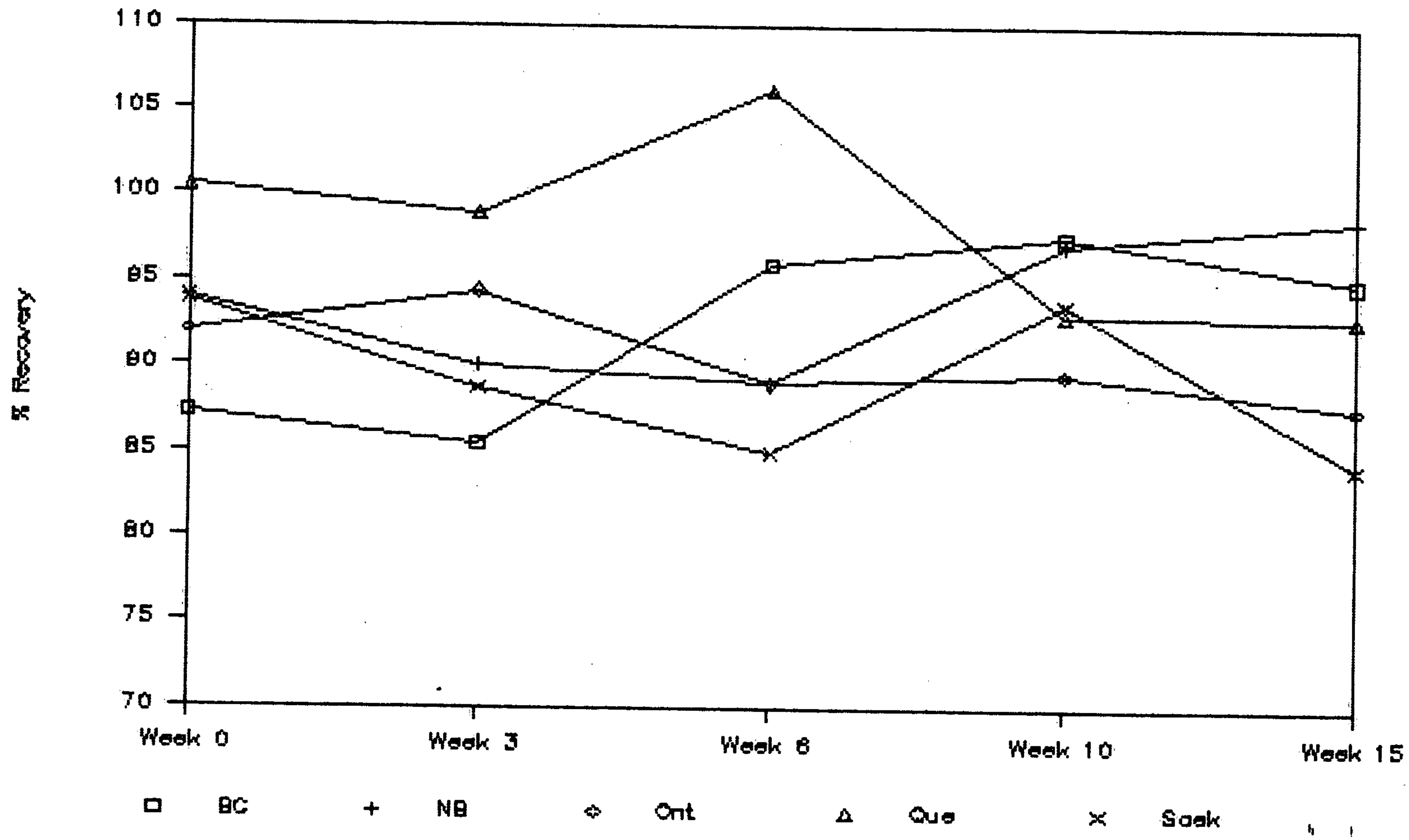

Fig. 7. Recovery of Dieldrin

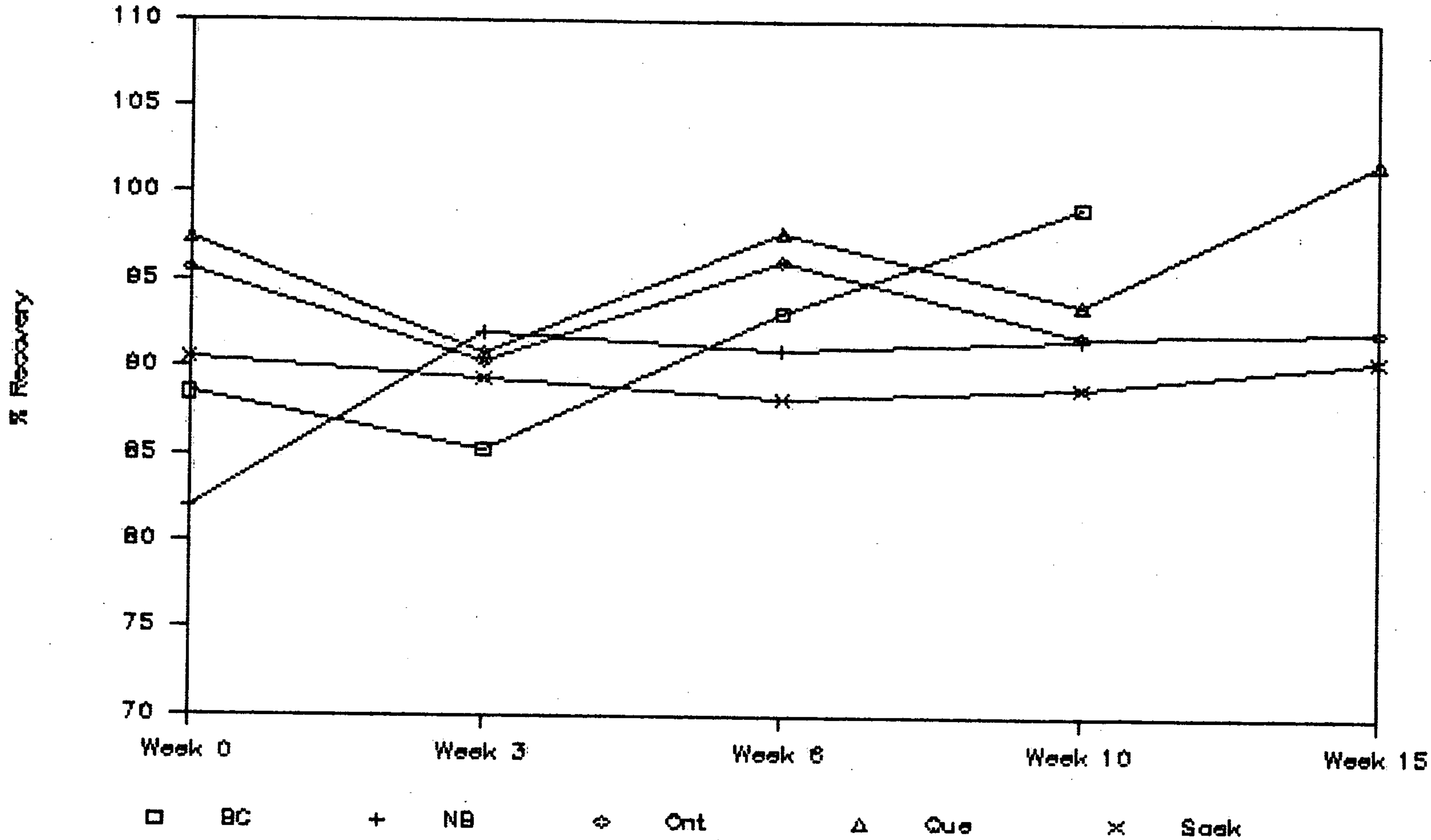

Fig. 8. Recovery of Endrin

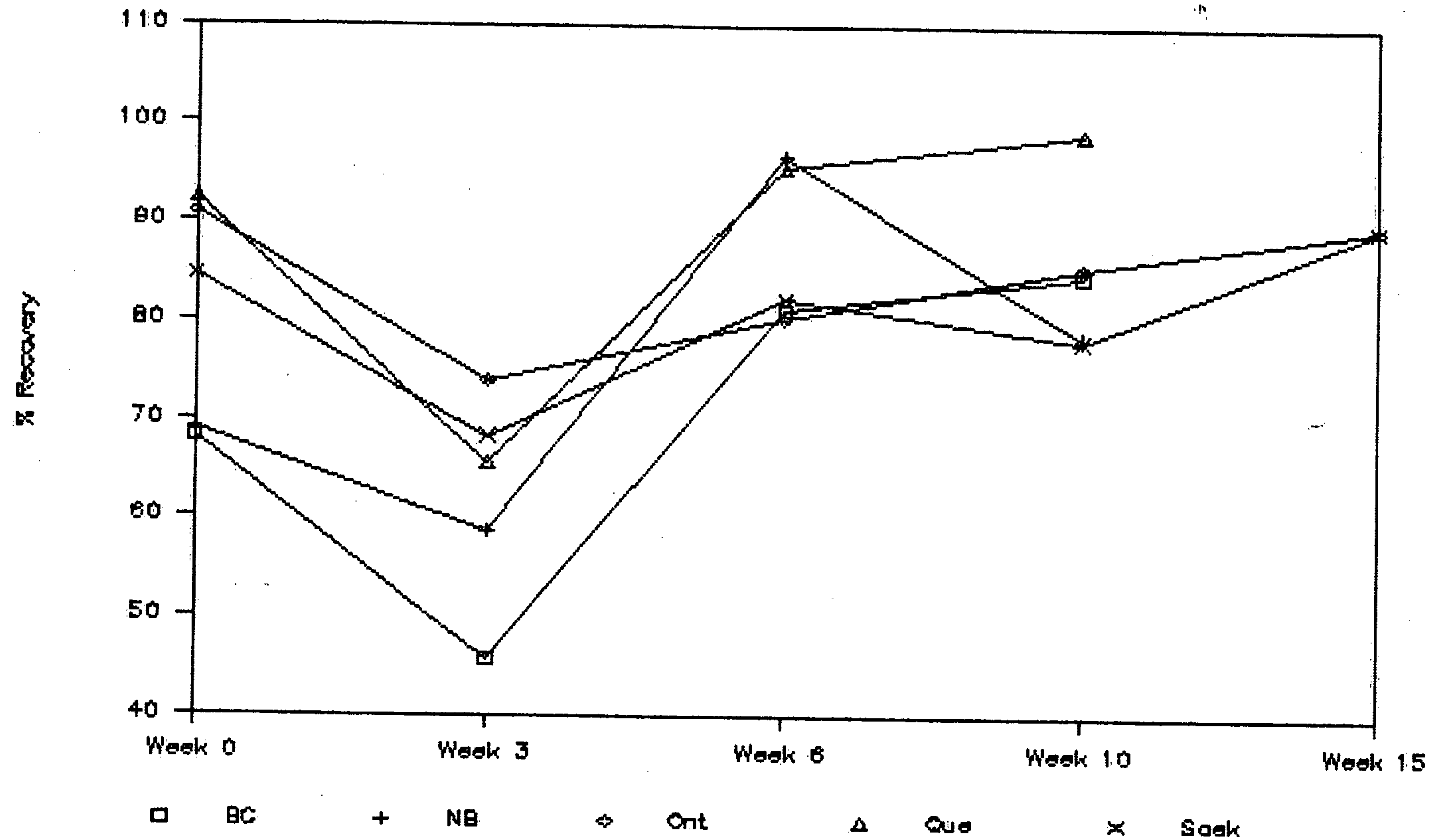

Fig. 9. Recovery of g-BHC

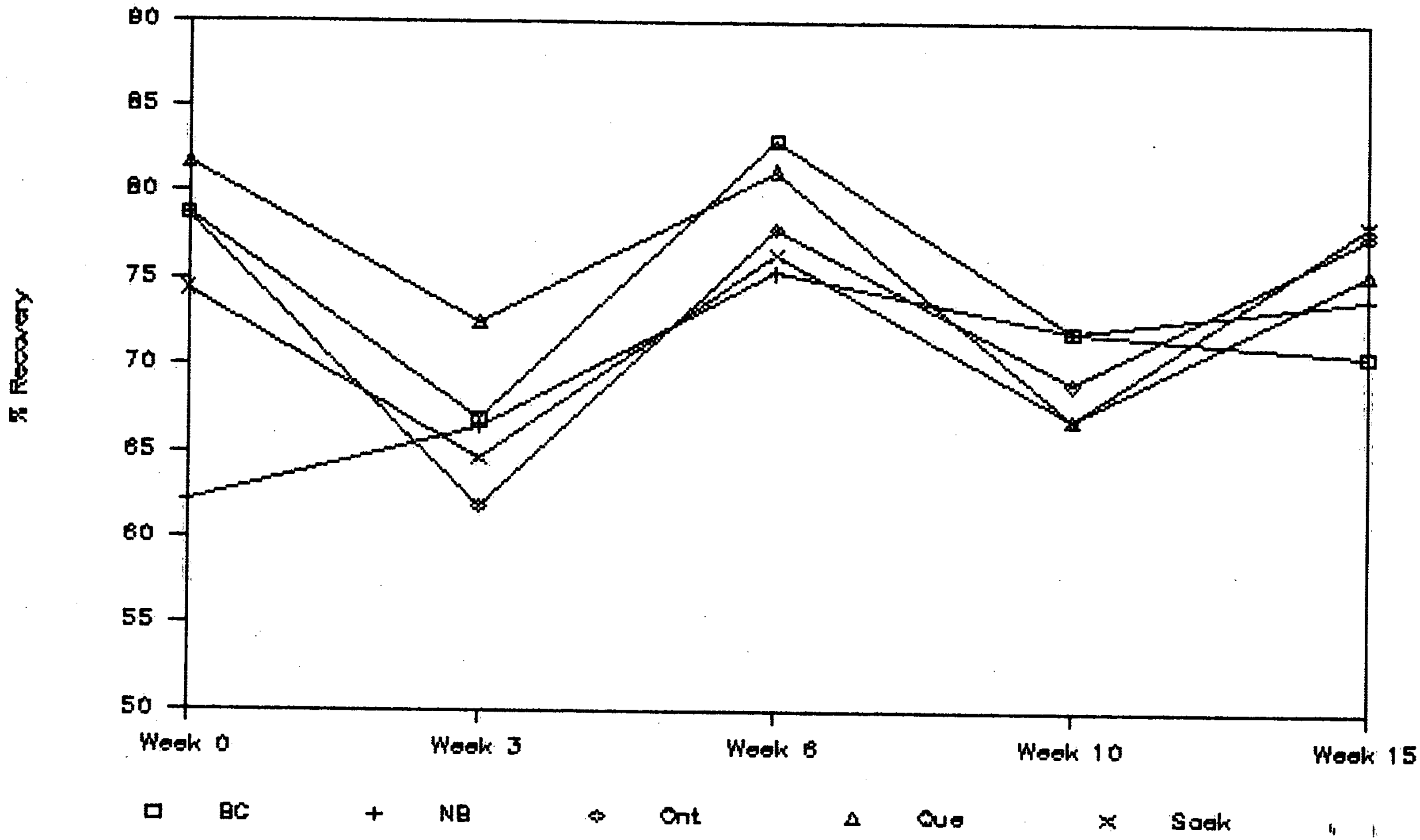

Fig. 10. Recovery of g-Chlordane

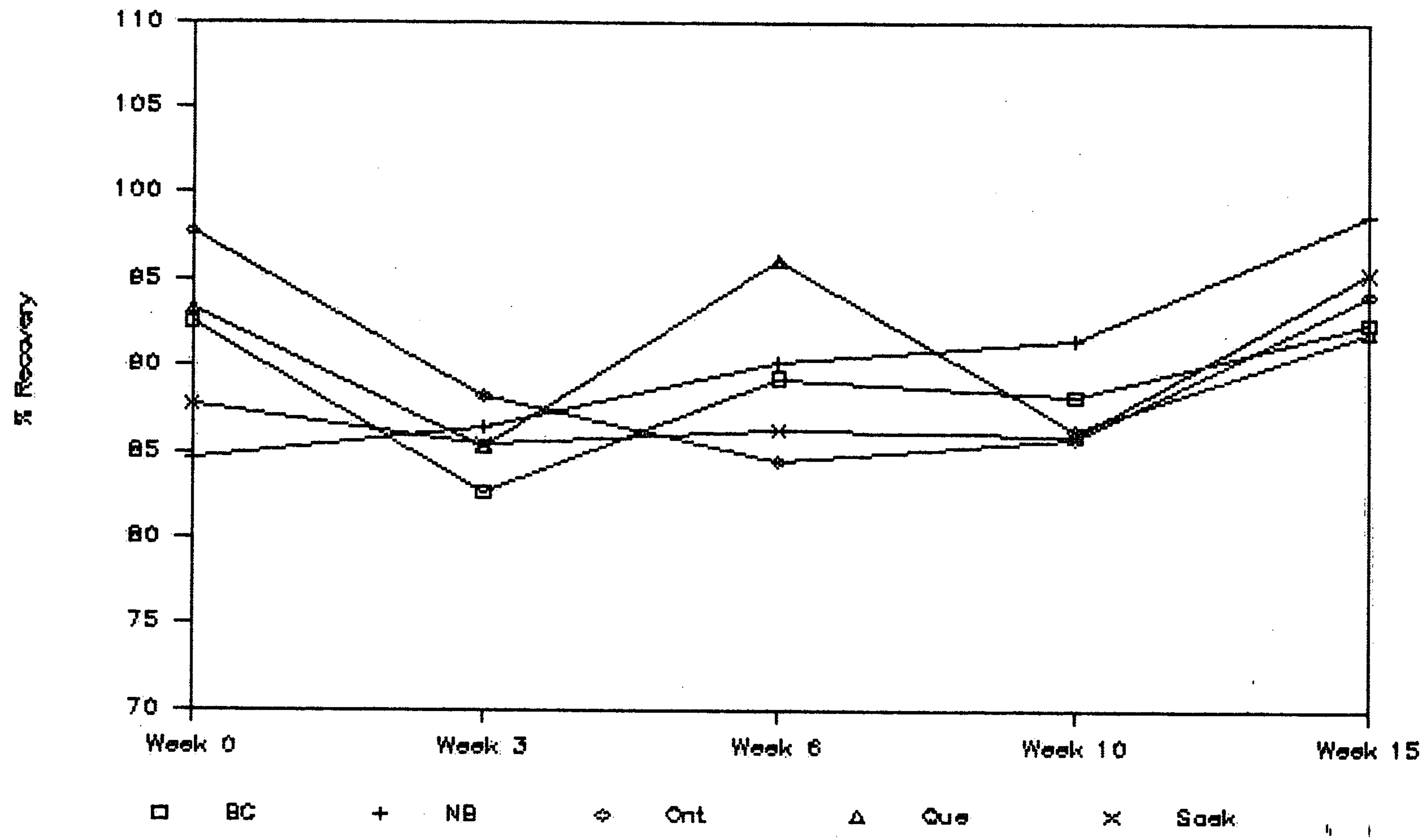

Fig. 11. Recovery of HCB

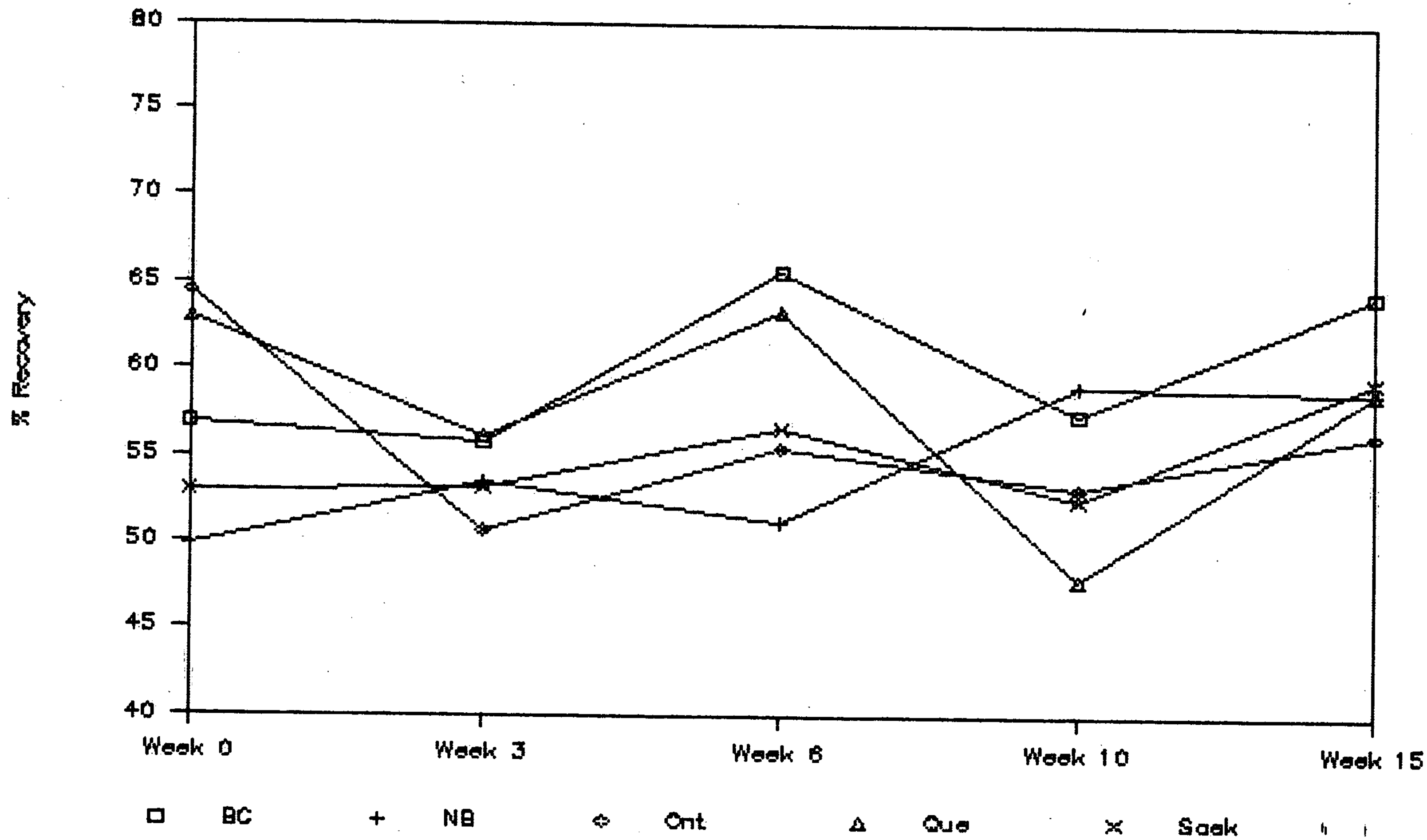

Fig. 12. Recovery of Heptachlor

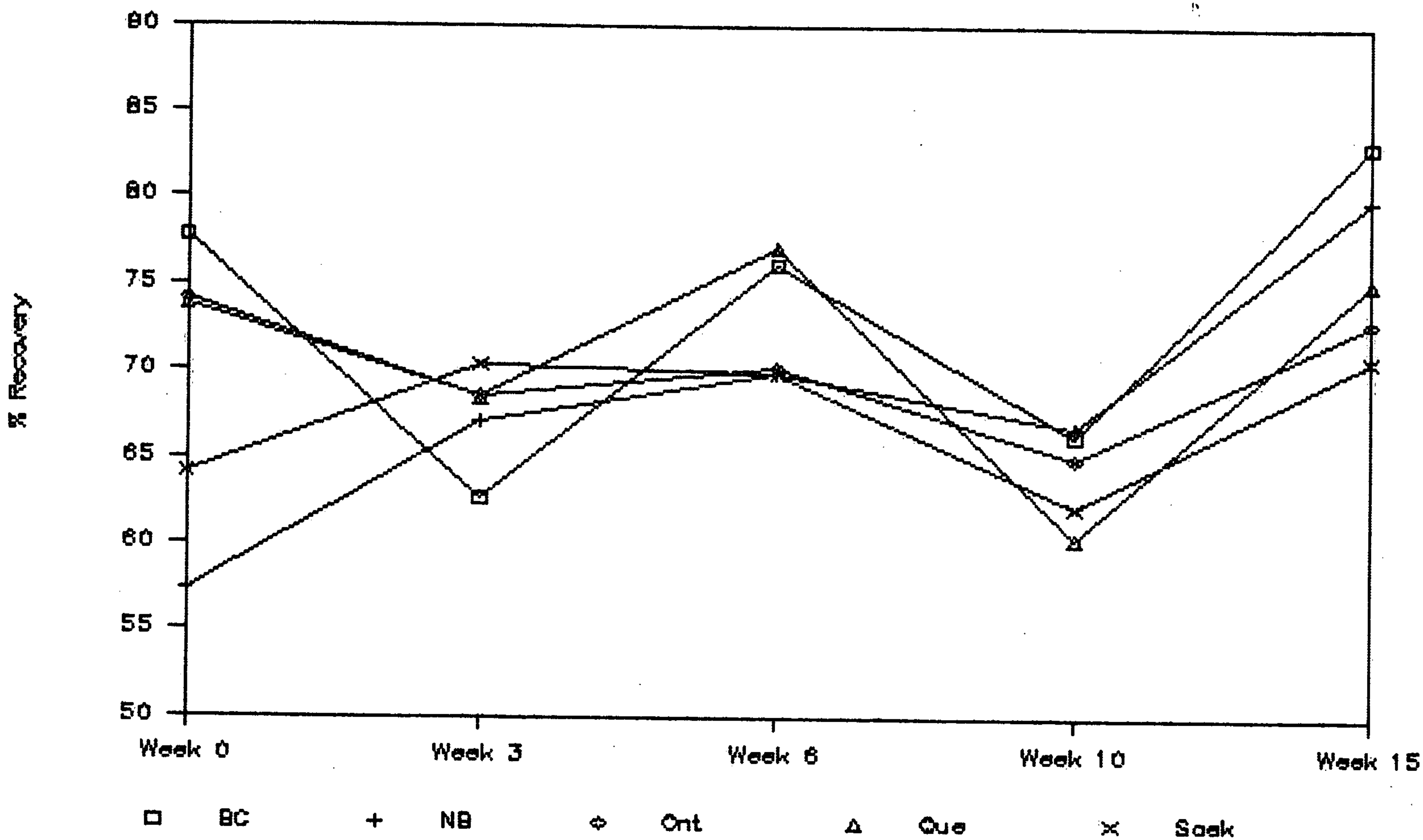

Fig. 13. Recovery of Heptachlor epoxide

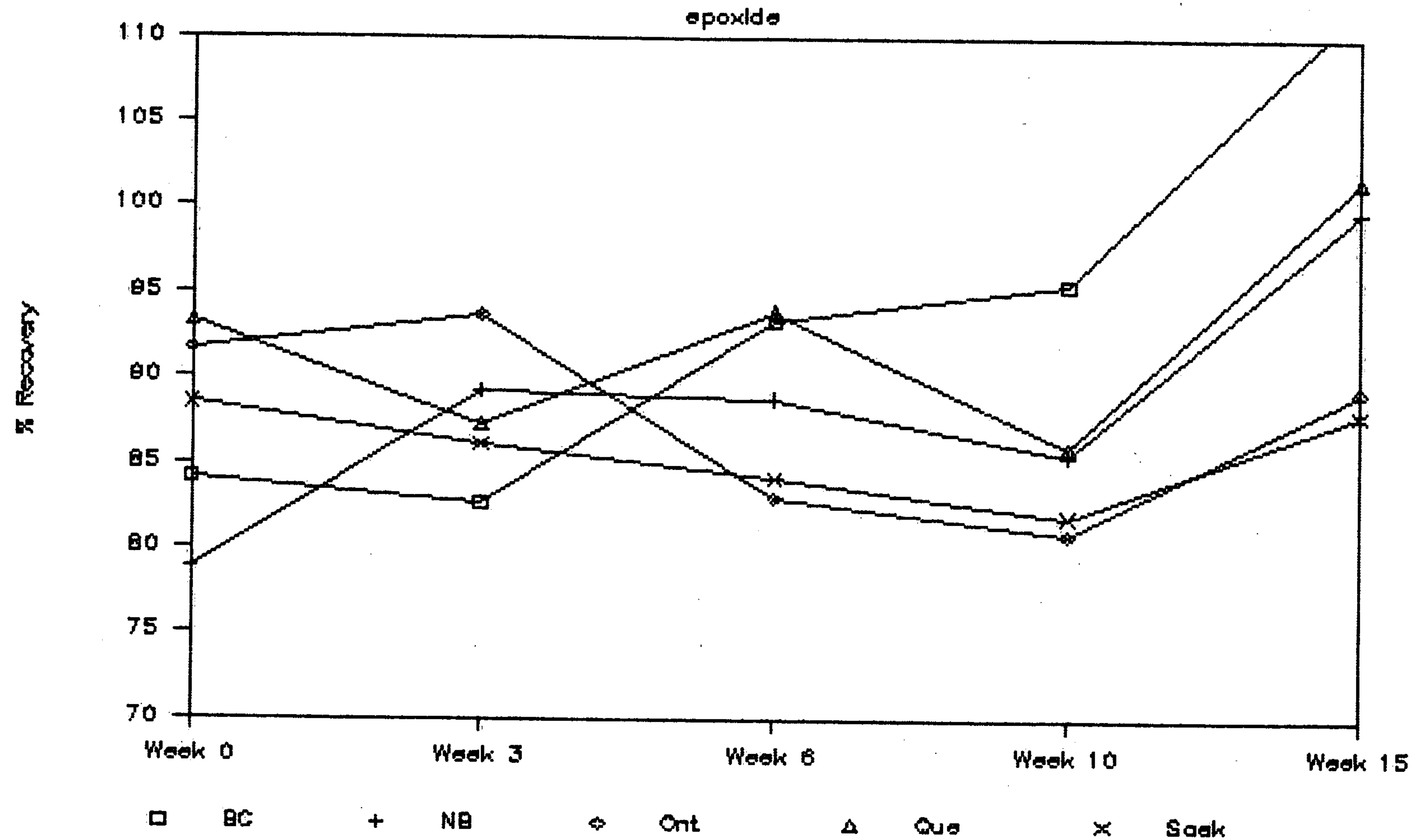

Fig. 14. Recovery of Methoxychlor

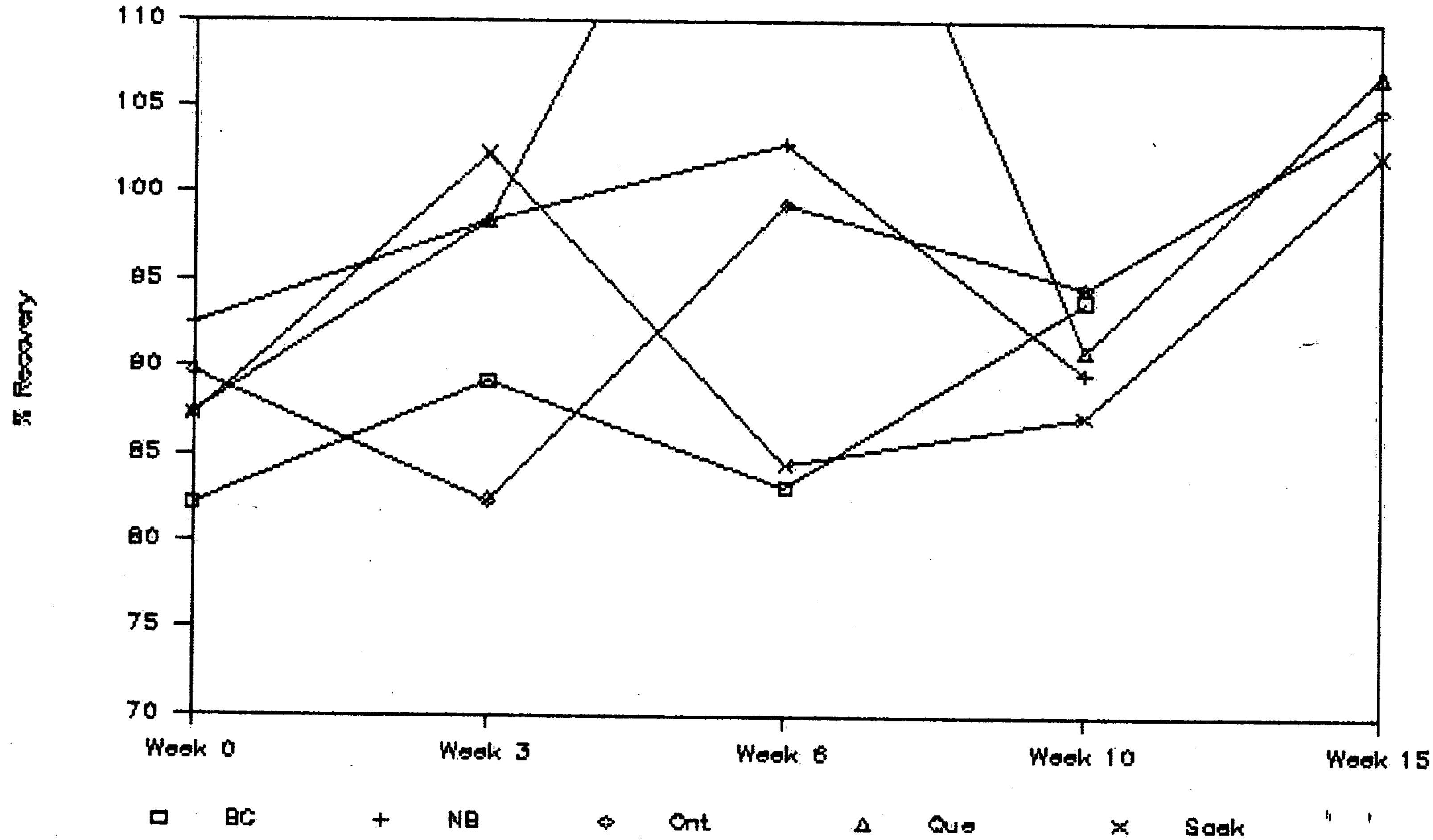

Fig. 15. Recovery of Mirex

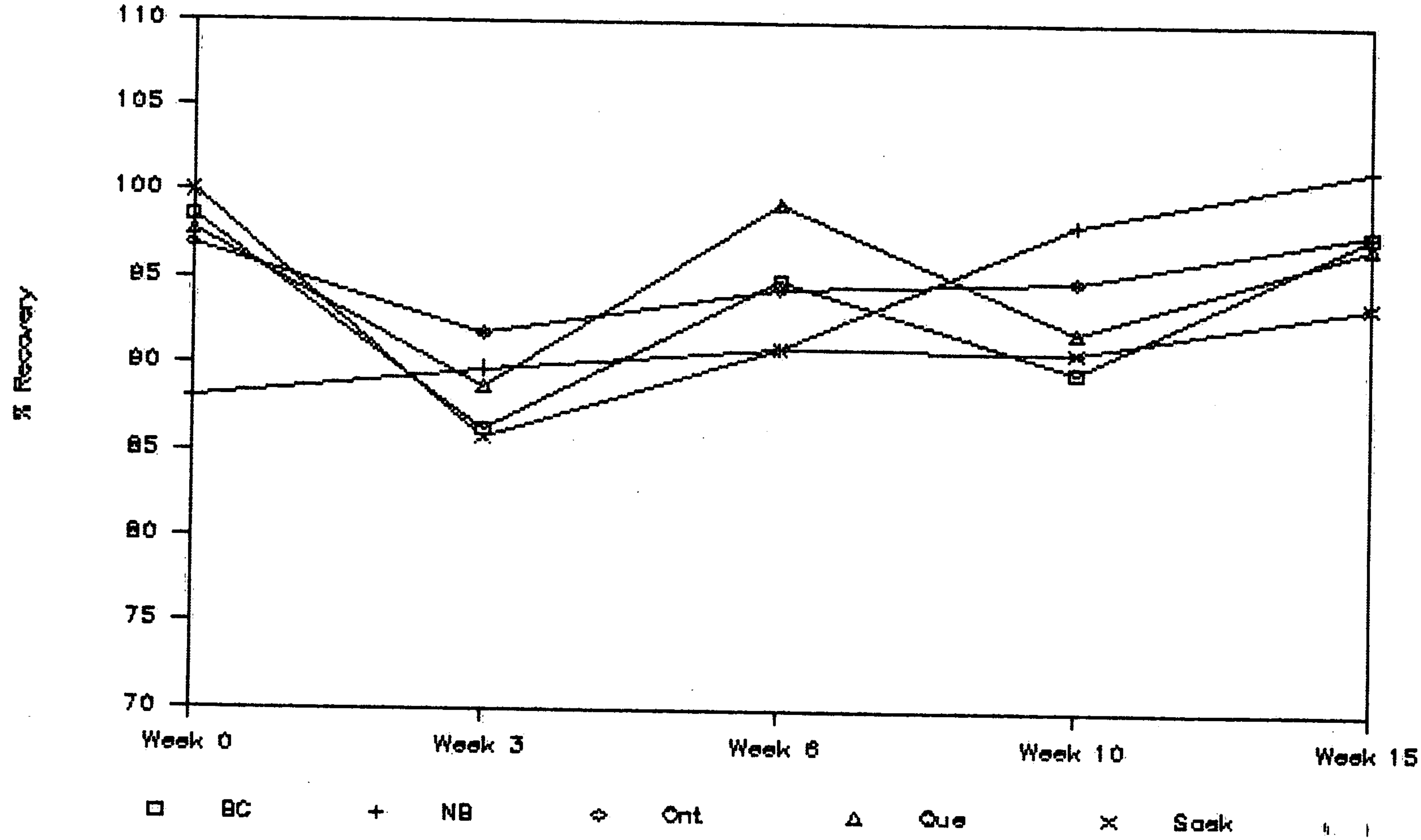

Fig. 16. Recovery of op'–DDT

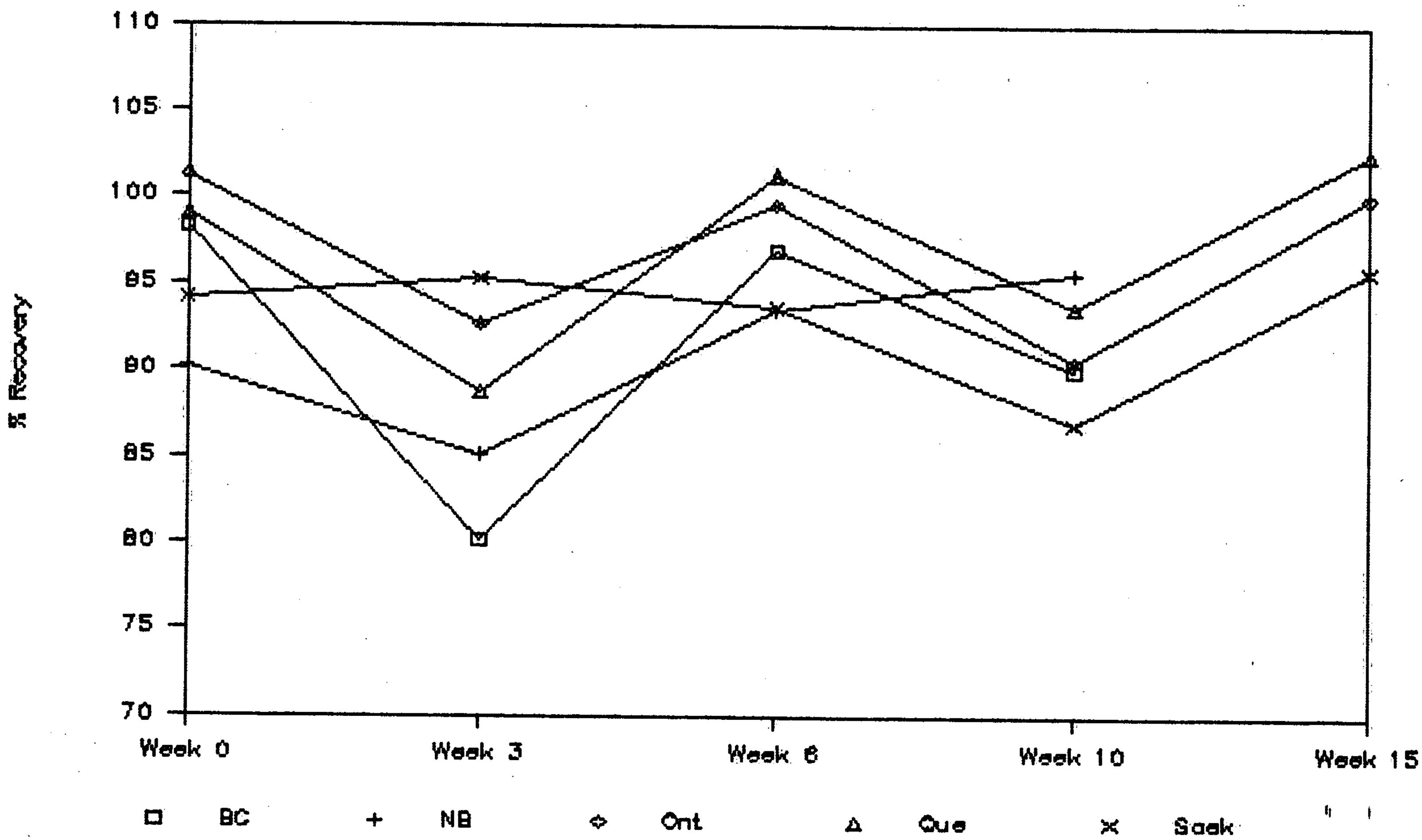

Fig. 17. Recovery of pp'–DDD

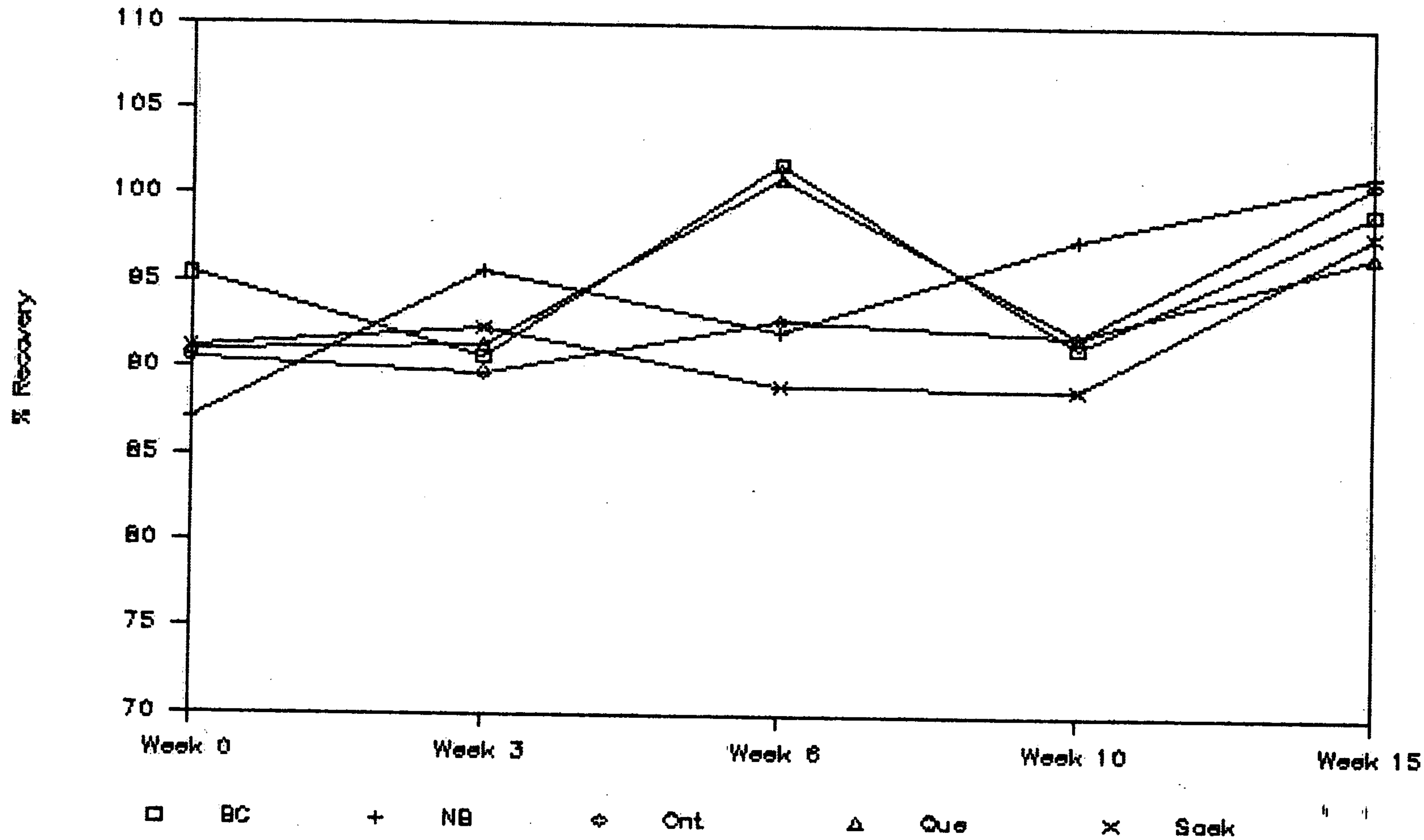

Fig. 18. Recovery of pp'—DDE

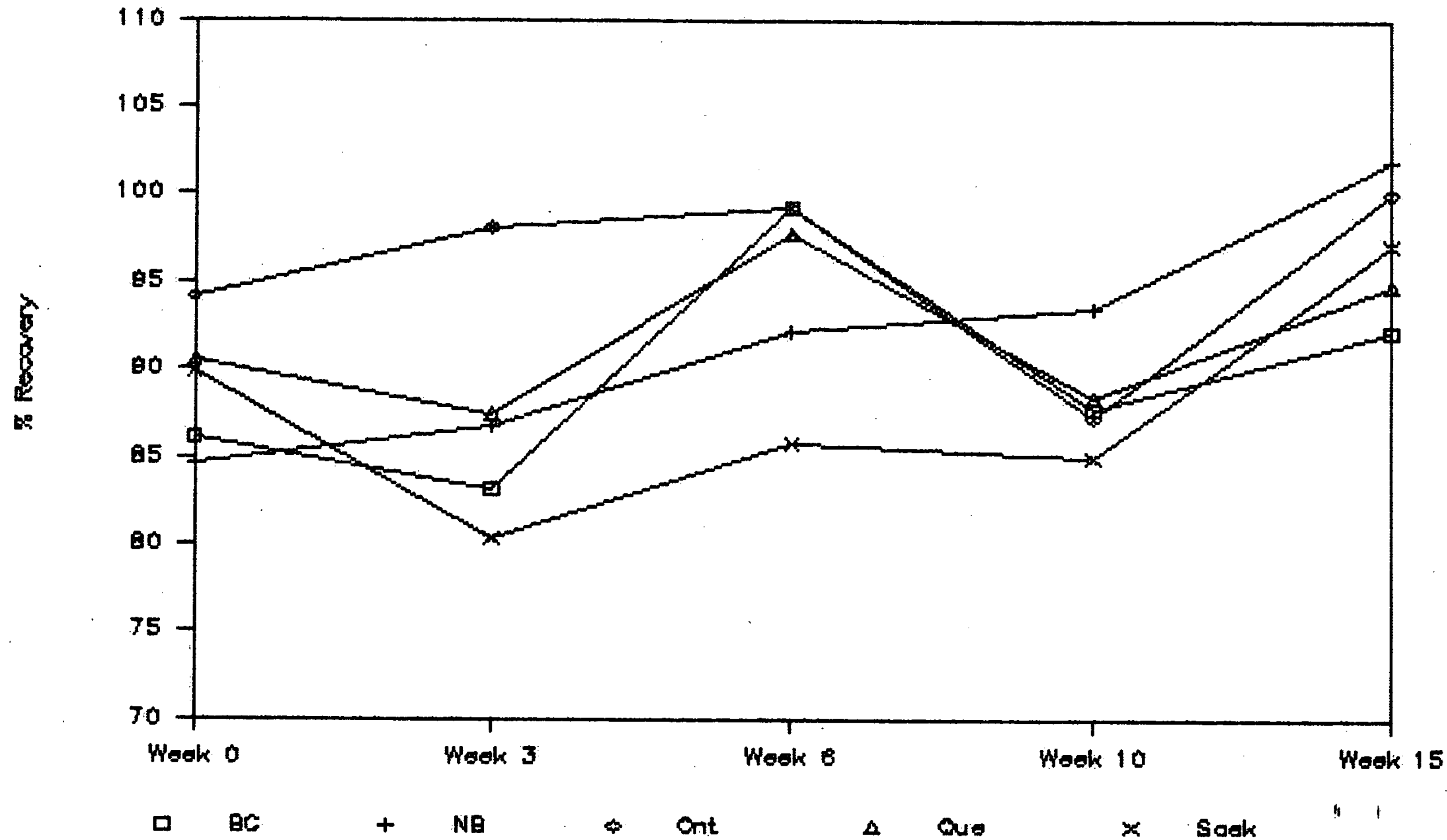

Fig. 19. Recovery of pp′-DDT