Variability of Pesticides in River Water and its Effect on Estimation of Load

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VARIABILITY OF PESTICIDES IN RIVER WATER AND ITS EFFECT ON ESTIMATION OF LOAD

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SUMMARY

The objectives of this study were to investigate the temporal variability of the concentrations of twelve Red List compounds, mainly pesticides, in the River Thames, and to compare the estimates of loads of these substances based on discrete data (grab samples and instantaneous measurements of flow) with those based on continuous monitoring.

The investigation was carried out using the continuous flow-proportional sampler previously established at Kingston upon Thames. Over a period of about a year a sequence of samples was taken from the flow-proportional sampler and a comparative sequence of grab samples at weekly intervals. Corresponding flow measurements were recorded. The samples were analysed for ten pesticides and two aromatic organic compounds on the Red List.

The data showed very strong temporal variations in flow, in the concentrations of most of the 12 substances and hence in the pollutant loads. A large proportion of the total load was discharged in a short period following the floods of 1990.

Estimates of annual load based on weekly grab samples differed from those achieved by continuous flow-proportional sampling by as much as ±50%. Confidence intervals for estimates based on discrete sampling were often very wide. These results confirm the conclusions of the previous report (PRS 2383-M), that methods of estimation based on discrete sampling suffer from large uncertainties associated with their inability to account fully for the temporal variations in concentration and flow, particularly because peaks can be inadequately represented or completely missed.

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SECTION 1 - INTRODUCTION

There is growing concern about the discharge of pollutants to the marine environment. Rivers provide an important route by which such substances may be conveyed to the sea. Rational discussion on the control of marine pollution therefore requires information on the sizes of river-borne loads and on the accuracy and precision with which these loads are estimated. Furthermore, any long-term trends in river-borne loads need to be assessed against short-term variations.

A previous study (Harrison et al 1990) concluded that the annual load of a given substance transported by a particular river can be most precisely estimated when the water discharge rate is measured continuously and the concentrations of the specified substance are obtained from a continuous series of composite samples taken by a flow-proportional sampler.

In practice, a less-costly sampling regime is generally undertaken, involving a small number of grab samples, spread periodically through the year. The concentrations found in these samples are combined with data on instantaneous flows (measured at the times when the grab samples are taken) to produce instantaneous loads. These may be averaged directly and grossed up to produce annual loads or allowance may be made for the total volume discharged during the year. However, uncertainties and difficulties are associated with this process because of temporal variations in concentration and flow and the vagaries of sampling.

The purpose of the present study was to establish the temporal variability of ten selected pesticides and two aromatic organic compounds on the Red List over a one-year period in the River Thames at Kingston upon Thames, and, for annual loads discharged to the estuary, to compare the accuracy and precision of estimates obtained by grab sampling with estimates obtained by flow-proportional sampling.

Signals from the ultrasonic gauge were fed to the controller which automatically activated the sampler when a specified volume of water had passed the gauging station. The sampler was set up to discharge 5 ml aliquots of river water into a 5 litre glass sample bottle at a frequency directly proportional to the volumetric discharge of the river. This meant that an aliquot was collected, on average, approximately every twenty minutes. The sample bottle was cooled to 4 °C by a thermostatically controlled bath.

Grab samples were taken at weekly intervals, on the final day of collection of the corresponding composite samples. They were collected into 5 litre sample bottles directly from the outlet of the sampling pump.

The instantaneous flow in the river was recorded whenever a grab sample was taken. The average flow was calculated for each interval over which a composite sample was collected.

2.2 SAMPLE PREPARATION

To obtain accurate analyses of the twelve selected substances at low concentrations, rigorous cleaning of apparatus was essential. The following procedure was adopted in this study. Glassware was initially washed thoroughly with tapwater. It was then rinsed with a detergent (Teepol) solution, followed by high purity Milli-Q water, and dried at 150-200 °C. The glassware was then repeatedly washed with acetone, followed by the extraction solvent (hexane or methanol) and dried in the oven. Immediately before use, all apparatus was further rinsed with the extraction solvent.

All organic solvents were of pesticide-grade or HPLC-grade (supplied by Rathburn). Anhydrous sodium sulphate was of Aristar grade and was dried at 500 °C for 4 hours, cooled and stored in a dessicator until required. Disposable florisil cartridges were obtained from Analytichem International.

The twelve compounds were:

lindane
aldrin
endrin
dieldrin
pp'DDE
pp'DDT
PCB (sum of three isomers)
hexachlorobutadiene
hexachlorobenzene
trifluralin
atrazine
simazine

The program of sampling and chemical analysis was carried out by the University of Essex under contract to WRc.

SECTION 2 - METHODS

2.1 SAMPLING

Samples were taken over the period 5 July 1989 to 28 August 1990 from the River Thames at a site adjacent to the existing river gauging station at Kingston upon Thames. The river discharge was measured by the Sarasota multi-path ultrasonic river gauge at the site, operated by the National Rivers Authority Thames Region.

Composite samples were collected over intervals of one week. They were taken by the flow-proportional sampler which had been specially designed by WRc for the previous study of methods of estimating loads (Harrison et al 1990). The intake of the high-volume plastic centrifugal pump was located approximately 3 m out from the right-hand bank at a depth of 2 m below high-water level. The inlet pipe was equipped with a coarse strainer and the pump was fitted with a fine strainer (1 mm gap) to protect the sampler. To avoid the settling of suspended solids, high flow velocities were maintained through the sampler.

Table 2 - Primary stock solutions: Weight per 100 ml of solvent

Standard	Weight mg	Solvent
1. γ-HCH	40	acetone
2. Aldrin	60	acetone
3. Endrin	60	acetone
4. Dieldrin	100	acetone
5. pp'DDE	100	acetone
6. pp'DDT	400	acetone
7. PCBs	10	acetone
8. Hexachlorobutadiene	200	acetone
9. Hexachlorobenzene	100	acetone
10. Trifluralin	60	methanol
11. Atrazine	40	methanol
12. Simazine	20	methanol
cis-Heptachlor Epoxide	60	acetone

2.2.1 Extraction of organochlorine insecticides and chlorinated aromatics

Unfiltered samples of 1 litre volume were extracted into 50 ml of hexane in a glass bottle placed on a mechanical shaker for 20 minutes. The sample was transferred into a 3 litre separating funnel and the two phases were allowed to separate for at least 5 minutes before the hexane was run into a glass container. The separating funnel was rinsed with a further 50 ml of hexane, and this solvent was used to repeat the extraction procedure. When complete, the walls of the separating funnel were rinsed with hexane and the washings added to the extract.

The hexane extract was dried by passing it through 30 g of anhydrous sodium sulphate, previously rinsed with hexane, supported by a sintered glass plug. After the extract had passed through, the sodium sulphate was rinsed with hexane and the washings were added to the extract. The dried extract was collected in a 250 ml round-bottom flask and evaporated on a steam bath to 5 ml ± 1 ml. The extract was then subjected to a clean-up procedure on a florasil disposable cartridge, previously prepared by rinsing with hexane. The florasil was then rinsed with hexane and the washings were added to the extract.

Standard chemicals, together with their purity and supplier are listed in Table 1. Primary stock solutions of each determinand were prepared by dissolving the weights shown in Table 2 in 100 ml of solvent. Appropriate dilutions were made to prepare analytical standards and spiked water samples for recovery studies.

Table 1 - Standards used in the chemical analysis

Standard	Purity %	Supplier
1. γ-HCH	99.7	LGC
2. Aldrin	99.5	LGC
3. Endrin	99.5	LGC
4. Dieldrin	99.5	LGC
5. pp'DDE	99.8	LGC
6. pp'DDT	99.8	LGC
7. PCBs (3 isomers)	99.0-99.7	BCR, Brussels
8. Hexachlorobutadiene	99.6	Greyhound Chromatography and Allied Chemicals
9. Hexachlorobenzene	99.9	LGC
10. Trifluralin	99.5	Greyhound Chromatography and Allied Chemicals
11. Atrazine	99.3	LGC
12. Simazine	99.9	LGC

Notes

The three PCB isomers were

2,2',4,5,5'	Pentachlorobiphenyl	(IUPAC No: 101)
2,2',3,4,4',5'	Hexachlorobiphenyl	(IUPAC No: 138)
2,4,4'	Trichlorobiphenyl	(IUPAC No: 138)

2.4 CALIBRATION

The electron capture detector (ECD) was calibrated by means of prepared standards corresponding to the range 0 - 10 ng l^{-1} in water. The calibration curve was linear over this range, which proved to be sufficient for all samples of river water, with one exception where simple dilution was required. Calibration of the ECD was frequently checked against standards and found to be stable.

The nitrogen-specific detector was calibrated over the range 0 - 100 ng l^{-1} in water. The calibration curve was linear over this range. Re-calibration was required twice per day.

Many problems were encountered with the TSD detector. The TSD bead was replaced twice during the course of the investigation, and as a result the performance changed. Originally, the detector was of exceptionally good sensitivity, although within the wide range of performance encountered with detectors. The first replacement bead was already well used and had a very poor performance. The third and final TSD bead was also not new and had a sensitivity well below that originally supplied, although still within specification. The detection limit achievable with this bead was around 5 ng l^{-1} (water concentration).

2.5 RECOVERY STUDIES, PROCEDURAL BLANKS AND INTERNAL STANDARDISATION

To assess possible losses during the analytical procedures, recovery experiments were carried out on using Milli-Q water blanks spiked with a known amount of standard taken from the primary stock solutions. For the earlier analyses, conducted by G Thorogood, the recovery percentages for each determinand are shown in Table 3. For the later analyses, conducted by A Sage, the recovery percentages are given in Table 4.

The dried and cleaned extract was concentrated further to 1 ml using a gentle stream of nitrogen and placing the extract in a calibrated vessel in a water bath at 40 °C. The prepared extract was stored in the dark at 4 °C until analysis.

2.2.2 Extraction of triazine herbicides and trifluralin

The following extraction procedure was carried out for trifluralin, atrazine and simazine. Unfiltered samples of 1 litre volume were rendered alkaline to a pH in excess of 8.0 using ammonia solution, before being extracted into 50 ml of dichloromethane by a mechanical shaker for 20 minutes. The sample was transferred into a 3 litre separating funnel. The aqueous phase was run off and the extract was discharged into a glass container. The funnel was rinsed with a further 50 ml of dichloromethane, which was subsequently added to the aqueous phase and the extraction procedure was repeated. The funnel was again rinsed after extraction and the washings were added to the mixed extract.

The mixed extract was dried by passing it through 30 g of anhydrous sodium sulphate, supported by a sintered glass plug. The sodium sulphate was rinsed with dichloromethane and the washings were added to the extract. The dried extract was collected in a 250 ml round-bottom flask and evaporated on a steam bath to 5 ml ± 1 ml. The extract was then subjected to a clean-up procedure on a disposable florasil cartridge, previously prepared by rinsing with dichloromethane. The florasil was rinsed with dichloromethane after use and the washings were added to the extract. The extract was then evaporated just to dryness with a gentle stream of nitrogen and the residue dissolved in 1 ml of methanol.

2.3 INSTRUMENTATION

Chemical analysis was performed on 1 ml concentrated extracts by a Varian 3500 gas chromatograph equipped with an electron capture detector (ECD) and a Nitrogen-Phosphorus (TSD) detector. A 60 m by 0.32 mm DB-5 column from J&W Scientific was used to separate the residues with nitrogen as the carrier gas.

A separate test was carried out to estimate procedural blank levels. The results are also presented in Table 4, in terms of equivalent concentration in the initial sample.

The compound, cis-heptachlorepoxide, was selected as an internal standard. This was introduced at a known concentration into the sample water before extraction. Unfortunately, it was found that the river water samples contained a substance co-eluting with the peak for cis-heptachlorepoxide. Since the quantities found were significant and varying, this had the effect of invalidating the internal standardisation. There was not enough time to investigate a substitute.

2.6 CALCULATIONS

The peak heights were measured on the chromatogram and the weight of each determinand was read from the calibration graphs. The concentrations, expressed in ng l^{-1}, were calculated according to the formula:

$$C = A \cdot v / V$$

where

A = weight of substance (pg) in the 1 µl portion of extract chromatographed;

v = final volume of extract (ml);

V = volume of sample (ml) from which the extract was taken.

The results were corrected for the efficiency of extraction as measured by the recovery studies.

Table 3 - Recovery from spiked blanks: Earlier analyses

		Concentration in spiking solution ng l^{-1}	Recovery %			Mean	S.D.
1.	γ-HCH	5.0	95	68	101	88	14.3
2.	Aldrin	7.5	68	62	67	66	2.6
3.	Endrin	7.5	74	71	77	74	2.4
4.	Dieldrin	12.5	69	67	67	68	0.9
5.	pp'DDE	12.5	71	61	63	65	4.3
6.	pp'DDT	12.5	75	75	76	75	0.5
7.	PCBs	10.0	64	60	61	62	1.7
8.	Hexachlorobutadiene	12.5	68	65	65	66	1.4
9.	Hexachlorobenzene	25.0	66	64	68	66	1.6
10.	Trifluralin	1.5	78	81	85	81	2.9
11.	Atrazine	50.0	54	65	60	60	4.5
12.	Simazine	25.0	79	64	71	71	6.1

Table 4 - Recovery from spiked blanks; Procedural blanks

		Recovery %					Mean	S.D.	Procedural Blank (ng l^{-1})
1.	Lindane	76	83	72	87	54	74	11.6	0.60
2.	Aldrin	82	96	90	94	82	89	5.7	0.16
3.	Endrin	94	50	54	50	54	60	17.1	0.35
4.	Dieldrin	57	33	35	31	37	39	9.1	0.00
5.	pp'DDE	71	83	78	82	77	78	4.1	0.20
6.	pp'DDT	72	88	85	88	80	83	5.7	0.13
7.	PCB1	74	84	82	96	79	83	7.4	1.00
	PCB2	91	97	96	96	93	94	2.2	0.20
	PCB3	90	98	95	98	98	96	3.2	0.32
8.	Hexachlorobutadiene	91	84	74	88	78	83	6.2	0.20
9.	Hexachlorobenzene	82	97	88	98	79	89	7.4	0.23
10.	Trifluralin	80	79	82	85	80	81	2.1	<d.l.
11.	Atrazine	55	58	62	64	54	58	3.8	<d.l.
12.	Simazine	65	65	71	64	73	67	3.6	<d.l.
	cis-Heptachlor Epoxide	67	71	83	82	86	78	7.6	

Table 5 - Flows (m^3 s^{-1}) and Concentrations of Determinands (ng l^{-1})

Sample number	Sample Interval	Sample Type	FLOW	Component Number and Code 1 LIND	2 ALDR	3 ENDR	4 DIEL
1	05 07 89 to	c	28.8	15.2	6.2	2.5	3.2
	13 07 89	g	15.0	6.3	6.4	1.9	3.3
2	13 07 89 to	c	34.2	16.9	5.6	2.4	3.0
	20 07 89	g	9.0	3.1	4.1	1.0	2.4
3	20 07 89 to	c	9.2	14.1	7.5	0.7	6.4
	27 07 89	g	5.0	6.8	5.6	3.6	2.6
4	27 07 89 to	c	7.4	2.5	2.1	0.4	2.1
	03 08 89	g	10.0	3.3	4.5	1.1	3.1
5	03 08 89 to	c	7.0	2.3	2.0	0.3	2.0
	11 08 89	g	17.0	6.5	6.0	2.0	3.8
6	11 08 89 to	c	6.7	2.3	2.0	0.6	2.4
	17 08 89	g	8.0	6.0	5.6	3.0	2.7
7	17 08 89 to	c	5.3	6.5	5.5	2.0	1.3
	24 08 89	g	6.0	6.6	5.3	2.4	1.65
8	24 08 89 to	c	9.1	13.1	12.0	1.3	3.0
	31 08 89	g	1.0	10.9	6.1	3.4	3.0
9	31 08 89 to	c	4.7	29.6	14.0	2.5	7.2
	08 09 89	g	1.0	26.8	16.8	3.4	6.4
10	08 09 89 to	c	4.3	27.4	7.37	4.2	8.4
	14 09 89	g	5.0	25.7	20.6	13.6	11.2
11	14 09 89 to	c	5.0	17.2	9.9	7.3	5.9
	21 09 89	g	5.0	13.5	13.5	7.6	6.2
12	21 09 89 to	c	5.9	23.6	23.3	10.7	15.9
	28 09 89	g	6.0	22.9	13.4	11.2	13.8
13	28 09 89 to	c	5.3	17.2	21.9	8.6	13.7
	05 10 89	g	3.0	20.6	20.3	13.2	13.2
14	05 10 89 to	c	7.1	15.9	21.9	6.9	8.4
	12 10 89	g	5.0	16.9	17.6	13.6	13.2

5	6	7	8	9	10	11	12
DDE	DDT	PCB	HCBD	HCB	3FLU	ATRA	SIMA
24.4	30.1	43.4	32.1	7.7	•	•	•
24.8	31.2	49.1	29.2	9.9	•	•	•
17.2	23.0	9.9	46.2	7.3	0.9	12.6	5.1
7.6	9.6	4.8	41.2	15.8	1.3	16.8	5.1
2.2	5.6	76.4	42.2	5.3	2.1	4.2	10.3
1.95	8.5	59.8	34.0	5.0	1.0	11.2	5.1
0.8	24.1	81.9	64.5	26.1	1.5	16.8	15.4
6.9	9.3	81.5	60.9	14.4	1.7	30.8	23.2
0.6	24.3	47.8	54.2	39.3	0.9	21.0	3.2
2.5	24.2	40.1	50.9	34.1	1.0	12.6	5.1
1.1	22.8	35.8	21.3	6.4	1.0	51.8	36.1
1.8	6.2	35.1	27.3	6.0	1.3	35.0	32.2
1.1	9.3	28.0	45.8	6.1	1.5	68.6	28.3
2.0	10.2	28.5	34.0	7.9	1.5	93.8	26.4
18.5	6.8	22.4	24.7	11.9	2.1	43.4	36.1
2.1	6.5	41.4	23.5	9.6	1.7	53.2	33.5
9.9	15.6	44.5	30.1	13.7	1.5	92.4	28.3
10.2	16.5	42.2	26.5	11.9	1.0	105.0	32.2
11.3	16.1	38.9	24.7	14.6	0.9	72.8	23.2
8.7	13.1	28.8	23.3	14.0	0.9	67.2	25.8
7.5	14.7	35.1	29.2	20.7	1.5	105.0	28.3
6.4	19.2	41.5	26.1	24.5	1.4	105.0	24.5
10.5	19.2	45.2	24.6	28.8	1.3	57.4	25.8
11.4	24.8	42.0	26.5	24.9	1.6	72.8	26.4
9.3	6.8	29.5	16.7	26.8	1.4	127.4	32.2
11.4	6.0	27.3	24.7	22.1	1.7	91.0	32.2
11.4	15.1	28.2	25.9	10.0	1.5	58.8	29.6
9.9	15.6	39.1	24.7	14.4	1.5	61.6	33.5

SECTION 3 - RESULTS

3.1 CONCENTRATIONS

Between 5 July 1989 and 28 August 1990, 49 composite samples were obtained from the flow-proportional sampler, as described in Section 2.1. Most sampling intervals lasted 7 days although there were a few 6-day and 8-day intervals. On two occasions, the sampling interval was about twice as long as usual. These were between 18 October 1989 and 3 November 1989 (16 days) and between 20 December 1989 and 3 January 1990 (14 days). Grab samples were taken at the end of each sampling interval.

There were three short periods when no composite samples were collected and no grab samples were taken. These were between 3 November 1989 and 16 November 1989 (13 days), between 12 January 1990 and 12 February 1990 (31 days) and between 12 March 1990 and 26 March 1990 (14 days).

Broken bottles caused the loss of the grab sample for 16 April 1990 and the composite sample for the interval 16 April 1990 to 23 April 1990.

The concentrations of the selected substances in the composite and grab samples are presented in Table 5. Unless specified otherwise, all concentrations in this report are given as ng l^{-1}. The substances are referred to by the following codes:

1	LIND	lindane
2	ALDR	aldrin
3	ENDR	endrin
4	DIEL	dieldrin
5	DDE	pp'DDE
6	DDT	pp'DDT
7	PCB	PCB (sum of three isomers)
8	HCBD	hexachlorobutadiene
9	HCB	hexachlorobenzene
10	3FLU	trifluralin
11	ATRA	atrazine
12	SIMA	simazine

Table 5 - continued

Sample number	Sample Interval	Sample Type	FLOW	Component Number and		
				1 LIND	2 ALDR	3 ENDR
29	02 04 90 to	c	*	4.14	0.33	0.34
	09 04 90	g	51.0	4.01	0.19	0.4
30	09 04 90 to	c	37.9	3.76	0.49	0.27
	16 04 90	g	43.0	*	*	*
31	16 04 90 to	c	*	*	*	*
	23 04 90	g	39.0	2.37	0.83	0.37
32	23 04 90 to	c	32.7	2.11	0.42	0.2
	01 05 90	g	37.0	1.82	0.33	0.13
33	01 05 90 to	c	*	1.35	0.83	0.41
	08 05 90	g	21.0	1.73	0.55	0.39
34	08 05 90 to	c	17.8	1.73	0.66	0.48
	15 05 90	g	21.0	1.73	0.15	0.53
35	15 05 90 to	c	17.3	1.82	0.44	0.39
	22 05 90	g	18.0	2.19	0.35	0.39
36	22 05 90 to	c	12.2	2.32	0.61	0.39
	29 05 90	g	11.0	2.13	0.49	0.39
37	29 05 90 to	c	12.5	2.18	0.33	1.11
	05 06 90	g	10.0	3.69	0.44	0.48
38	05 06 90 to	c	9.1	3.66	0.36	0.48
	12 06 90	g	9.0	2.38	0.33	0.44
39	12 06 90 to	c	8.8	2.63	0.29	0.44
	19 06 90	g	11.0	2.19	0.33	0.48
40	19 06 90 to	c	7.5	1.82	0.35	0.48
	26 06 90	g	5.0	2.19	0.29	0.48
41	26 06 90 to	c	10.4	1.88	0.33	0.48
	03 07 90	g	6.0	1.88	0.22	0.48
42	03 07 90 to	c	6.3	2.0	0.22	0.48
	10 07 90	g	7.0	1.46	0.55	0.55

Code								
4	5	6	7	8	9	10	11	12
DIEL	DDE	DDT	PCB	HCBD	HCB	3FLU	ATRA	SIMA
1.12	0.24	0.93	1.28	5.71	3.92	34.5	48.2	97.0
0.79	0.21	0.76	0.91	1.99	4.55	N.D.	109.0	544.5
2.17	0.2	0.79	1.12	2.86	5.99	N.D.	158.0	795.2
*	*	*	*	*	*	N.D.	*	*
*	*	*	*	*	*	*	*	*
2.09	1.13	10.33	1.21	1.99	4.09	*	*	*
1.21	0.35	0.46	0.72	5.80	6.01	*	240.0	973.5
1.43	0.3	1.95	0.66	1.68	3.99	N.D.	132.0	795.5
1.42	0.24	0.52	0.68	1.79	3.99	N.D.	163.0	620.5
0.83	0.24	0.46	0.66	1.9	4.31	N.D.	135.6	230.0
0.79	0.24	0.41	1.06	2.1	5.66	N.D.	260.5	989.0
0.53	0.24	0.39	1.04	0.64	3.99	N.D.	141.5	680.0
0.82	0.3	14.79	1.28	0.97	3.55	N.D.	250.5	890.0
1.98	0.21	3.05	1.12	2.1	4.22	N.D.	240.0	750.0
1.48	0.36	86.4	1.81	1.96	6.55	N.D.	256.0	809.0
1.93	0.18	2.19	1.33	1.63	4.09	N.D.	245.0	74.4
1.42	0.3	0.46	1.24	0.81	2.80	N.D.	347.3	252.7
1.82	0.21	1.1	1.55	0.93	4.88	N.D.	329.1	172.9
1.5	0.24	0.76	1.59	1.75	5.87	N.D.	306.7	227.4
1.42	0.18	1.5	1.52	2.34	4.22	N.D.	134.1	107.0
1.42	0.18	0.64	1.03	1.34	5.11	N.D.	239.4	434.6
1.67	0.21	0.64	1.41	0.93	4.88	N.D.	220.3	401.2
1.45	0.35	0.46	1.95	1.15	4.96	N.D.	306.2	534.9
1.09	0.36	0.52	1.51	1.69	4.88	N.D.	300.0	534.9
1.12	0.18	0.46	1.36	0.15	4.44	N.D.	315.8	595.0
1.45	0.35	0.52	1.56	0.15	5.55	N.D.	347.7	635.2
0.79	0.24	2.72	2.25	0.23	5.87	N.D.	195.0	252.0
2.09	0.24	0.82	2.34	0.15	5.33	N.D.	204.0	267.3

Table 5 - continued

Sample number	Sample Interval	Sample Type	FLOW	Component Number and		
				1 LIND	2 ALDR	3 ENDR
15	12 10 89 to	c	5.1	29.6	14.0	6.9
	18 10 89	g	2.0	35.6	19.8	13.1
16	18 10 89 to	c	7.1	11.7	12.7	4.9
	03 11 89	g	5.0	17.4	20.6	8.0
17	16 11 89 to	c	6.2	28.8	16.8	9.1
	23 11 89	g	5.0	27.4	24.6	8.5
18	23 11 89 to	c	7.1	20.6	13.9	7.3
	30 11 89	g	11.0	22.8	20.9	6.9
19	30 11 89 to	c	7.1	22.5	5.2	3.1
	07 12 89	g	10.0	27.4	6.0	3.8
20	07 12 89 to	c	10.2	27.7	5.4	2.4
	14 12 89	g	71.0	24.0	6.9	2.5
21	14 12 89 to	c	57.9	40.0	7.3	4.2
	20 12 89	g	122.0	34.7	4.8	1.2
22	20 12 89 to	c	231.5	48.6	5.0	2.0
	03 01 90	g	60.0	31.8	3.2	1.0
23	04 01 90 to	c	57.9	35.2	1.7	<d.l.
	12 01 90	g	64.0	44.5	2.8	<d.l.
24	12 02 90 to	c	296.0	31.1	3.6	3.4
	19 02 90	g	210.0	57.7	4.0	2.0
25	19 02 90 to	c	72.0	47.6	2.5	1.8
	26 02 90	g	64.0	11.0	1.4	0.6
26	26 02 90 to	c	180.0	7.7	5.2	<d.l.
	05 03 90	g	179.0	8.9	3.7	<d.l.
27	05 03 90 to	c	105.0	30.6	6.2	1.1
	12 03 90	g	91.0	28.8	4.5	<d.l.
28	26 03 90 to	c	47.0	2.38	0.11	0.27
	02 04 90	g	51.0	4.64	0.22	0.27

Code 4 DIEL	5 DDE	6 DDT	7 PCB	8 HCBD	9 HCB	10 3FLU	11 ATRA	12 SIMA
8.9	18.7	15.2	43.4	16.3	19.2	2.1	51.8	34.8
16.6	16.7	13.0	42.5	20.2	14.4	1.9	42.0	30.9
9.1	18.2	15.6	35.0	17.1	24.7	1.6	57.4	33.5
7.7	17.8	16.1	40.7	25.5	22.3	1.7	57.4	29.6
5.8	7.0	13.1	35.0	16.7	19.2	1.5	91.0	28.3
6.3	8.6	15.8	27.3	16.7	16.2	1.5	95.2	24.5
5.1	9.1	7.0	29.5	14.7	14.0	2.6	92.4	26.4
5.5	8.3	14.6	21.8	24.6	13.6	1.5	105.0	27.7
7.2	3.2	16.0	33.2	23.4	9.1	2.8	68.6	27.0
6.9	4.4	19.5	44.8	22.5	11.2	3.3	95.2	23.2
7.1	2.4	22.6	59.	33.2	6.0	1.5	51.8	20.6
7.7	4.5	16.	43.3	28.8	11.2	0.9	43.4	15.4
4.5	3.7	17.8	52.9	97.5	16.4	1.6	33.6	18.0
3.8	6.0	14.7	76.4	56.9	12.7	1.6	49.0	18.0
3.5	4.1	19.25	29.5	76.7	23.7	*	*	*
2.9	5.1	15.1	35.7	28.8	12.3	*	*	*
1.1	7.0	13.5	44.7	57.7	12.4	*	*	*
2.7	7.2	9.2	43.4	55.8	12.0	*	*	*
<d.l.	6.4	12.7	39.1	22.7	23.1	20.8	139.8	51.2
5.1	6.8	10.5	25.1	27.3	27.8	4.1	117.7	86.6
4.7	5.1	4.	20.	67.2	13.6	4.1	33.2	19.8
2.1	6.0	3.5	29.1	17.9	6.8	N.D.	5.98	29.1
4.4	7.0	5.5	23.7	10.0	5.7	N.D.	9.31	6.39
4.8	8.6	4.3	18.4	9.1	13.9	N.D.	43.2	39.0
<d.l.	3.2	12.2	56.8	23.9	<d.l.	*	*	*
2.5	2.4	8.1	52.9	28.6	<d.l.	*	*	*
0.82	0.18	0.46	0.39	2.1	2.79	27.3	24.1	20.1
0.9	0.24	1.17	0.91	3.32	2.99	2.9	142.3	251.3

3.2 RIVER FLOW

The fourth column of Table 5 gives average flow rates over each sampling interval and instantaneous flow rates measured at the time when the grab sample was taken. There were no average flow results for the sampling intervals commencing 2 April 1990, 16 April 1990 and 1 May 1990 because of logger failure. Flows are given throughout this report as $m^3\ s^{-1}$.

SECTION 4 - TEMPORAL VARIATION

4.1 FLOW

The variation in flow over the period of the study is shown in Figure 1. Day 1 is 1 July 1989. The horizontal parts of the crenellated line graph show the average flow over each sampling interval, and the vertical parts connect the end of each interval with the beginning of the next. Sloping lines indicate periods over which no data were available. Instantaneous flow measurements are indicated by asterisks at the end of each sampling interval.

The results in Table 5 and Figure 1 show some extremely high flows in the period from 14 December 1989 to 12 March 1990 (Day 167 to Day 255). Some of the worst flooding of the River Thames for many years occurred in this period, with the peak occurring in week commencing 5 February 1990. Unfortunately, no samples could be taken in the period 12 January 1990 to 12 February 1990 when the highest flows of all would have been recorded. After 12 March 1990, there was a steady decline in flow, settling down to around 4 $m^3\ s^{-1}$ in July and August.

The pattern of variation of flow with time shows three distinct phases: the low flows in the summer and autumn of 1989, the very high flows in the winter, followed by the period of low and still lower flows in spring and summer 1990. Although the division between the second and third of these phases is somewhat arbitrary, we have chosen dividing dates of 14 December 1989 and 12 March 1990 to enable comparisons to be

Table 5 - continued

				Component Number and Code											
Sample number	Sample Interval	Sample Type	FLOW	1 LIND	2 ALDR	3 ENDR	4 DIEL	5 DDE	6 DDT	7 PCB	8 HCBD	9 HCB	10 3FLU	11 ATRA	12 SIMA
43	10 07 90 to	c	6.0	1.5	0.76	0.27	1.45	0.24	0.46	1.74	0.46	4.66	N.D.	245.3	334.0
	17 07 90	g	4.0	1.0	0.33	0.48	0.96	0.24	0.46	2.19	0.23	4.11	N.D.	152.9	186.9
44	17 07 90 to	c	7.9	1.63	0.33	0.48	0.88	0.3	0.58	1.14	0.58	5.38	N.D.	21.3	46.5
	24 07 90	g	4.0	1.38	0.33	0.41	0.96	0.21	0.52	1.09	0.52	5.11	N.D.	<d.l.	<d.l.
45	24 07 90 to	c	3.9	1.38	0.22	0.48	0.8	0.18	0.46	1.04	0.29	4.05	N.D.	21.3	23.2
	31 07 90	g	3.0	0.62	0.21	0.41	1.12	0.18	0.41	1.04	0.23	3.88	N.D.	19.1	23.2
46	31 07 90 to	c	4.1	1.57	0.66	<d.l.	0.83	0.12	0.46	1.79	1.4	6.66	N.D.	8.5	11.9
	07 08 90	g	3.0	1.19	0.33	<d.l.	0.32	0.12	none	1.39	3.16	4.05	N.D.	21.3	23.2
47	07 08 90 to	c	3.5	1.11	0.31	<d.l.	0.32	0.12	5.87	2.08	7.26	6.61	N.D.	8.5	11.9
	14 08 90	g	3.0	0.94	0.66	<d.l.	0.51	0.24	0.82	2.92	0.76	3.88	N.D.	29.8	23.2
48	14 08 90 to	c	4.2	1.63	0.45	0.29	0.32	0.42	2.7	1.82	4.68	5.69	N.D.	7.8	33.9
	21 08 90	g	3.0	1.57	0.49	0.25	0.79	0.42	1.96	1.82	4.33	4.99	N.D.	54.6	90.4
49	21 08 90 to	c	4.5	3.57	0.32	0.013	0.4	0.48	4.69	2.24	2.28	6.27	N.D.	25.5	23.2
	28 08 90	g	3.0	1.63	0.22	0.013	0.4	0.37	0.79	1.71	5.56	4.55	N.D.	21.3	23.2

Notes:

c	composite sample;	g	grab sample;		
<d.l.	less than detection limit;	N.D.	not detectable;	*	missing value.

Table 7 - Average concentrations over the three periods

Period	Mean Conc (ng l^{-1})	Period	Mean Conc (ng l^{-1})
Lindane		PCB	
A	16.7	A	39.1
B	33.6	B	40.7
C	2.2	C	1.4
Overall	13.2	Overall	22.9
Aldrin		HCBD	
A	10.7	A	30.0
B	4.6	B	48.6
C	0.4	C	2.2
Overall	5.2	Overall	20.9
Endrin		HCB	
A	4.3	A	16.4
B	1.9	B	12.6
C	0.4	C	5.1
Overall	2.2	Overall	10.8
Dieldrin		Trifluralin	
A	6.3	A	1.6
B	3.2	B	5.6
C	1.1	C	3.1
Overall	3.5	Overall	2.8
DDE		Atrazine	
A	9.6	A	61
B	4.9	B	54
C	0.3	C	164
Overall	4.7	Overall	109
DDT		Simazine	
A	15.8	A	25
B	13.5	B	24
C	6.0	C	380
Overall	11.1	Overall	194

Key:

Period	Dates
A	5-JUL-1989 to 14-DEC-1989
B	14-DEC-1989 to 12-MAR-1990
C	12-MAR-1990 to 28-AUG-1990
Overall	5-JUL-1989 to 28-AUG-1990

made between the concentrations of the substances measured during these three different states of flow. The three periods will be referred to as A, B and C and their details are set out in Table 6.

Table 6 - Average flow over the three periods

Period	Dates	Mean Flow (m^3 s^{-1})
A	5 July 1989 to 14 December 1989	9
B	14 December 1989 to 12 March 1990	138
C	12 March 1990 to 28 August 1990	13
Overall	5 July 1989 to 28 August 1990	35

4.2 CONCENTRATIONS

Graphs of concentrations of the substances against time are presented in Figures 2.1 to 2.12, taking 1 July 1989 as Day 1. The results from composite samples are displayed as a crenellated line graph; the horizontal parts of the line show the average concentration over each sampling interval, and the vertical parts connect the end of each interval to the beginning of the next. Sloping lines indicate periods over which no data were available, either because no samples were collected or no analytical results were obtained. Results from grab samples are indicated by points (asterisks) at the end of each sampling interval. When drawing the graphs, values reported as 'less than the detection limit ' or 'not detected' were plotted as if they were zero.

The average concentrations in relation to the three periods of time corresponding to different stages of flow (Section 4.1) are set out in Table 7. The results in the table are strongly suggestive of real differences in concentration between the different periods. Formal

4.3 LOADS

For each of the twelve substances, the average load over each sampling interval was obtained by calculating the product of the concentration in the composite sample and the average flow over the sampling interval, and converting the result to kg per week.

The results are illustrated in Figures 4.1 to 4.12, using a crenellated line for the average load over each interval. The average loads in relation to the three periods A, B and C are set out in Table 8.

The points (asterisks) on the graphs represent instantaneous estimates of load, expressed as kg per week, obtained using the concentrations in the grab samples and the associated instantaneous flows. They are presented for comparison purposes, and will be referred to in Section 5. However, the remainder of this section deals only with the average loads, as defined in the previous paragraph.

With the exception of trifluralin, atrazine and simazine, it is readily apparent that average loads were much higher in period B than in the periods before and after. The simazine loads were also high in period B compared with period A but the high loads were maintained in period C until around 17 July 1990 (Day 382). Atrazine was similar except that the continuation of high loads into the third period was less marked. Trifluralin was not detected after 9 April 1990 (Day 283) and the loads are plotted at zero.

Analysis of variance techniques were again used to evaluate the statistical significance of differences in load between periods. The general conclusion that there were significant differences in nearly all cases should come as no surprise in view of the way in which load is derived from concentration and flow.

The average load in each period (Table 8) when multiplied by the length of the period would give the mass of compound conveyed during that period. It will be apparent that in spite of the relatively short duration of period B, it accounts for a large proportion of the total load conveyed over the duration of the study. This is illustrated in Figure 5.

statistical analyses (using analysis of variance of the logarithm of concentration) were undertaken to check whether these differences could be attributed to sampling fluctuations. The results of these analyses are summarised as follows.

For the six organochlorine insecticides (lindane, aldrin, endrin, dieldrin, DDE, DDT) and the three chlorinated aromatics (PCB, HCBD and HCB) the concentration in the third period was significantly lower than in the first two periods. Furthermore, lindane and aldrin (but not endrin, dieldrin, DDE, DDT, PCB, HCBD and HCB) had significantly different concentrations in the first two periods.

For trifluralin, there was one peak concentration in period B and two in period C, but the remainder of results in period C were below the detection limit. With such limited information, no conclusions about systematic changes in concentration can be drawn.

For atrazine, no significant differences were found between the concentrations in the three periods. For simazine, periods A and B were not significantly different from each other, but period C was significantly higher than both.

As flow itself is one of the factors which influences concentration, by several different but interdependent mechanisms, it is relevant to examine the relationship between concentration of each compound and flow. We have chosen to do this using the composite sample concentrations and the weekly average flows. The results are shown in this way in Figures 3.1 - 3.12.

In this presentation, different plotting symbols have been used for the three periods. The results are strongly suggestive of different physical relationships prevailing in the three periods earlier defined.

SECTION 5 - COMPARISON OF METHODS OF ESTIMATING LOAD

5.1 SUMMARY OF THE METHODS

Walling and Webb (1985) described a number of methods for estimating the load of a substance transported by a river. This study restricts itself to the three methods described in the previous report by Harrison et al (1990) to which reference should be made for a fuller description.

Section 4 in the present report has emphasised the systematic differences in the state of the river corresponding to weather and seasonal conditions. In the year when this study was undertaken these differences were particularly marked. The methodology of estimating load, however, makes no use of this information but assumes that the instantaneous measurements (of flow and load) can be regarded as drawn from statistical populations that do not change with time. This assumption is less crucial for the estimates themselves than for their confidence limits, a point to which we return in Section 6.2.

Method 1

Where there is a continuous record of flow, and concentrations are derived from flow-proportional composite samples taken over n successive intervals, the average load over those n intervals is calculated by the formula:

$$M_1 = \mathrm{mean}(L_i)$$

where the mean is taken over the values of i running from 1 to n and L_i is the average load over the i^{th} interval, calculated by

$$L_i = C_i \cdot Q_i$$

Table 8 - Average loads over the three periods

Period	Mean Load (kg week^{-1})	Period	Mean Load (kg week^{-1})
Lindane		PCB	
A	0.09	A	0.20
B	2.98	B	2.90
C	0.02	C	0.01
Overall	0.60	Overall	0.62
Aldrin		HCBD	
A	0.05	A	0.18
B	0.38	B	4.06
C	0.003	C	0.02
Overall	0.09	Overall	0.84
Endrin		HCB	
A	0.02	A	0.08
B	0.16	B	1.45
C	0.003	C	0.04
Overall	0.04	Overall	0.32
Dieldrin		Trifluralin	
A	0.03	A	0.01
B	0.21	B	0.82
C	0.01	C	0.04
Overall	0.06	Overall	0.12
DDE		Atrazine	
A	0.07	A	0.23
B	0.43	B	5.93
C	0.002	C	1.46
Overall	0.11	Overall	1.42
DDT		Simazine	
A	0.10	A	0.10
B	1.16	B	2.34
C	0.05	C	4.23
Overall	0.28	Overall	2.19

Key:

Period	Dates
A	5-JUL-1989 to 14-DEC-1989
B	14-DEC-1989 to 12-MAR-1990
C	12-MAR-1990 to 28-AUG-1990
Overall	5-JUL-1989 to 28-AUG-1990

$l_i = c_i \cdot q_i$,

c_i is the concentration in the i^{th} grab sample taken,

q_i is the instantaneous flow at the i^{th} instant of sampling,

and MEAN(Q) is the continuous average flow over the whole period of the study.

In this formula MEAN(Q) is time-weighted but mean(l_i) and mean(q_i) are simple averages. The formula is exactly equivalent to:

$M_2 = c_w \cdot \mathrm{MEAN(Q)}$

where c_w is the flow-weighted mean concentration of the grab samples, calculated by the formula

$c_w = \mathrm{mean}(q_i \cdot c_i) / \mathrm{mean}(q_i)$

or, identically,

$c_w = \mathrm{mean}(l_i) / \mathrm{mean}(q_i)$.

Hence, c_w is the quotient of two averages, each subject to sampling fluctuation. Confidence limits for M_2 can therefore be calculated by Fieller's method. These may be infinitely wide where the mean flow is small compared with its standard error. Further discussion of the statistical aspects of this method are given by Harrison et al (1990) who show that M_2 is a biased estimate, but that the bias should be small compared with other sources of error.

Method 3

Using only instantaneous measurements, there is the simpler unadjusted formula

$M_3 = \mathrm{mean}(l_i)$

where

C_i is the concentration in the flow-proportional composite sample collected over the i^{th} interval, and

Q_i is the average flow during the i^{th} interval.

As the n intervals of time in this study were of unequal length the calculation of mean(L_i) made allowance for this by time-weighting.

Since the temporal variability in the concentration and in the flow is integrated into C_i and Q_i, there should be negligible error in the estimate M_1 arising from these temporal fluctuations. The load is effectively measured continuously. Thus, M_1 is not subject to sampling uncertainty and confidence limits to take account of this are not appropriate.

M_1 will still be subject to other uncertainties arising from analytical errors, errors in the measurement of flow and imperfect mixing across the section of the river, discussed elsewhere (Harrison et al 1990). However, these uncertainties will affect equally all three methods discussed in this section, and so will not affect the relative merits of the methods.

Method 2

Where there is a continuous record of flow, but concentrations are derived only from grab samples, a common method of estimating mean load is to take the mean of the instantaneous loads and adjust it for mean flow over the period of the record. The appropriate formula is

$$M_2 = \text{mean}(l_i) \ . \ \text{MEAN}(Q) \ / \ \text{mean}(q_i)$$

where l_i is the instantaneous load at the i^{th} instant of sampling, calculated by

For the compounds other than trifluralin, the confidence intervals associated with M_2 and M_3 did, for most data sets, contain the 'correct' M_1 value. Where this did not happen the margin of failure was fairly narrow in most cases, with the exception of the bimonthly M_3 for endrin. The results therefore confirm that the estimates M_1, M_2 and M_3 are generally consistent with each other within the bounds of statistical error.

It must, however, be admitted that in these examples the bounds of statistical error are fairly wide. Methods 2 or 3, even when using the full set of weekly data, show examples of confidence intervals whose width is comparable with the size of the mean being estimated. This corresponds to estimation of mean load only to within ± 50%. Examples in the table, for instance for DDT, show that the agreement between M_1 and M_2 or M_3 can be as poor as that. For the subsets based on lower frequencies of sampling (monthly, bimonthly) it is easy to find examples where the confidence interval stretches from near zero to more than double the estimate of the mean.

For trifluralin most of the estimates based on discrete sampling were significantly lower than, and hence inconsistent with, M_1. This outcome can be attributed to the peculiar form of the trifluralin data. If concentration exhibits a small number of narrow peaks against a very low background level (Fig 2.10) no method of estimation based on grab sampling can offer reliable results.

The 95% confidence intervals for Method 2 were infinite for monthly and bimonthly sampling, for all twelve substances. This was not surprising, given the high variability in flow over the year and the low sampling frequency, and reflects the low precision achievable in these circumstances. The corresponding confidence intervals for Method 3 in these cases were also very wide.

which estimates the mean load over the period as the straightforward average of the instantaneous loads.

If these instantaneous loads are viewed as a simple random sample from the statistical distribution of instantaneous loads, then M_3 is unbiased and its standard error is simply estimated as the sample standard deviation of the loads l_i divided by the square root of the number of samples. A confidence interval for M_3 can then be calculated in the usual way.

5.2 COMPARISON OF THE THREE METHODS

Comparisons of the three methods were based on sampling frequencies representing weekly, fortnightly, monthly and bimonthly sampling. For weekly sampling every available grab sample was included in the calculations.

To provide realistic examples of what would happen in practice if lower rates of sampling were used, subsets were selected by stepping in regular intervals through the set of available grab samples. For fortnightly sampling every second sample was included starting at the second sample, for monthly every fourth sample was selected starting at the fourth sample, and for bimonthly every eighth sample starting at the seventh sample. The starting points were chosen at random, by rolling an eight-sided die.

For each subset selected in this way, estimates of mean loads and 95% confidence limits were calculated by Methods 2 and 3. The results of the calculations are presented in Table 9 and in graphical form in Figures 6.1 to 6.12.

Not surprisingly these estimates of load exhibit some differences between the results of the three different methods and between the results of using the same method on subsets of the data selected with different frequencies of sampling. In order to make some general observations on these results it is helpful to deal separately with trifluralin; the results for the other eleven compounds were broadly similar to each other.

Table 9 - continued

Estimate	95%LCL	Mean	95%UCL	Estimate	95%LCL	Mean	95%UCL
DDE				Atrazine			
M1		0.112		M1		1.419	
M2 1wk	0.059	0.106	0.134	M2 1wk	1.244	1.860	2.695
M2 2wk	0.	0.119	0.152	M2 2wk	0.800	1.914	3.486
M2 4wk	*	0.102	*	M2 4wk	*	2.308	*
M2 8wk	*	0.093	*	M2 8wk	*	3.023	*
M3 1wk	0.027	0.084	0.140	M3 1wk	0.533	1.294	2.054
M3 2wk	0.	0.108	0.219	M3 2wk	0.230	1.677	3.124
M3 4wk	0.	0.101	0.258	M3 4wk	0.	2.287	4.968
M3 8wk	0.	0.056	0.171	M3 8wk	0.	0.478	1.548
DDT				Simazine			
M1		0.278		M1		2.188	
M2 1wk	0.120	0.181	0.238	M2 1wk	1.385	3.092	6.383
M2 2wk	0.056	0.172	0.278	M2 2wk	0.716	2.853	10.602
M2 4wk	*	0.195	*	M2 4wk	*	3.349	*
M2 8wk	*	0.183	*	M2 8wk	*	4.500	*
M3 1wk	0.062	0.142	0.222	M3 1wk	0.833	2.151	3.469
M3 2wk	0.020	0.157	0.295	M3 2wk	0.429	2.500	4.570
M3 4wk	0.	0.193	0.452	M3 4wk	0.	3.320	7.000
M3 8wk	0.	0.110	0.269	M3 8wk	0.	0.711	2.789

Note: * indicates 95% confidence interval is unlimited

Table 9 - Estimates of mean load (kg/week) over period of study, with confidence limits

Estimate	95%LCL	Mean	95%UCL	Estimate	95%LCL	Mean	95%UCL
Lindane				PCB			
M1		0.598		M1		0.624	
M2 1wk	0.098	0.487	0.728	M2 1wk	0.323	0.611	0.862
M2 2wk	0.	0.534	0.980	M2 2wk	0.200	0.465	0.668
M2 4wk	*	0.734	*	M2 4wk	*	0.496	*
M2 8wk	*	0.518	*	M2 8wk	*	0.523	*
M3 1wk	0.048	0.382	0.717	M3 1wk	0.169	0.479	0.789
M3 2wk	0.	0.488	1.150	M3 2wk	0.062	0.425	0.787
M3 4wk	0.	0.728	2.061	M3 4wk	0.	0.492	1.127
M3 8wk	0.	0.310	1.037	M3 8wk	0.	0.313	1.017
Aldrin				HCBD			
M1		0.094		M1		0.838	
M2 1wk	0.059	0.079	0.099	M2 1wk	0.254	0.487	0.686
M2 2wk	0.053	0.085	0.131	M2 2wk	0.067	0.388	0.616
M2 4wk	*	0.081	*	M2 4wk	*	0.456	*
M2 8wk	*	0.049	*	M2 8wk	*	0.658	*
M3 1wk	0.030	0.062	0.095	M3 1wk	0.133	0.382	0.631
M3 2wk	0.019	0.078	0.137	M3 2wk	0.022	0.354	0.687
M3 4wk	0.	0.080	0.181	M3 4wk	0.	0.452	1.095
M3 8wk	0.	0.029	0.071	M3 8wk	0.	0.394	1.303
Endrin				HCB			
M1		0.040		M1		0.317	
M2 1wk	0.014	0.026	0.041	M2 1wk	0.085	0.258	0.361
M2 2wk	0.008	0.031	0.072	M2 2wk	0.	0.326	0.466
M2 4wk	*	0.038	*	M2 4wk	*	0.379	*
M2 8wk	*	0.010	*	M2 8wk	*	0.180	*
M3 1wk	0.008	0.020	0.032	M3 1wk	0.040	0.202	0.364
M3 2wk	0.004	0.028	0.052	M3 2wk	0.	0.298	0.633
M3 4wk	0.	0.038	0.085	M3 4wk	0.	0.376	1.012
M3 8wk	0.	0.006	0.013	M3 8wk	0.	0.108	0.294
Dieldrin				Trifluralin			
M1		0.055		M1		0.116	
M2 1wk	0.050	0.077	0.093	M2 1wk	0.	0.028	0.052
M2 2wk	0.036	0.092	0.115	M2 2wk	0.	0.034	0.075
M2 4wk	*	0.097	*	M2 4wk	*	0.056	*
M2 8wk	*	0.053	*	M2 8wk	*	0.012	*
M3 1wk	0.023	0.060	0.097	M3 1wk	0.	0.020	0.044
M3 2wk	0.010	0.084	0.159	M3 2wk	0.	0.030	0.078
M3 4wk	0.	0.096	0.221	M3 4wk	0.	0.056	0.150
M3 8wk	0.	0.032	0.073	M3 8wk	0.	0.002	0.006

The pattern of variation of concentration with time was different for different substances. The concentrations of the organochlorine insecticides and the chlorinated aromatics fell after the period of high flow in the winter, whilst that for the herbicide simazine increased. There were no significant trends in atrazine, and trifluralin was not detected in the later stages of the study.

The persistent low values found for the chlorinated insecticides and aromatics in the later part of the study led to the start of sampling for suspended solids, which were found to be very low indeed. This finding may explain the very low levels of these compounds which tend to be adsorbed on suspended material. There were no data on suspended solids in the earlier part of the study when concentrations were higher, so it was not possible to confirm a relationship between the concentrations of suspended solids and these substances.

It is possible that the floods and the associated high flows may have had the effect of flushing these compounds out of the system, and that the later lack of rainfall may have resulted in very little addition of these substances to the river as a result of run-off. In contrast the increases in the concentrations of atrazine and simazine after the floods may have been caused by the application of these herbicides in the new growing season. In addition, these two compounds are expected to behave differently from the other substances investigated as they are more mobile in soils and less strongly adsorbed. Given the problems with the chemical analysis reported in Section 2 and the extreme weather and flow conditions during the study period, it may be worthwhile investigating these two herbicides further. Further work is certainly needed before conclusions can be drawn with any confidence about the variation in trifluralin.

Since load is the product of flow and concentration, this unusual pattern of flows produced a very skewed distribution of loads. A large proportion of the total load over the year was discharged in the comparatively short period of high flows. Unfortunately, no samples were taken during a four week period at the peak of the floods, so it is likely that an important contribution to the annual loads passed unrecorded.

For Method 3, the bimonthly confidence limits were tighter than those for monthly sampling. This was surprising at first sight, but closer investigation revealed that this was due to the vagaries of sampling and the extremely high flows experienced in the winter. The bimonthly subset had only one sample point from the winter high flow period, and its flow value was fortuitously low. The monthly subset had two high flows including the peak flow of the year. This resulted in an extremely high instantaneous load, a large estimate for the standard deviation of load and hence the confidence interval wider than for the bimonthly set.

SECTION 6 - DISCUSSION

6.1 TEMPORAL VARIATION

Flow patterns during the period of the study were not at all typical of the River Thames. The winter produced the worst flooding for many years. In contrast, the summer and autumn of 1989 and the spring and summer of 1990 experienced exceptionally low rainfall. Consequently, apart from the period of extremely high flow in the winter, flow was uniformly low.

The chemical analyses of the samples were not subjected to as secure a quality control as desired, because there were a number of practical and logistic difficulties that could not have been foreseen. The internal standard that was selected proved to be ineffective because of the presence of interfering compounds in the river water. The TCD detector of the gas chromatograph required two replacement beads, neither of which was as satisfactory in terms of performance as the original. There were unanticipated changes in personnel during the study - three different people carried out extractions and two carried out analyses. It was not possible to compare the performance of the two analysts directly since they were not working simultaneously.

6.3 CROSS-RIVER VARIABILITY

The previous study (Harrison et al 1990) concluded that lack of homogeneity of concentration across the section of the river at the sampling site was not a serious problem for the substances investigated, namely nitrate, total phosphorus, soluble reactive phosphorus and the metals, Pb and Cu. Although some differences were found to be statistically significant, they were not consistent in two separate sampling exercises undertaken at different dates, one in spring and one in autumn. From the limited scale of the investigation, it was considered safe to conclude that if differences did exist they were unlikely to be greater than 20% of the mean cross-sectional concentration.

Although these conclusions were not drawn for the same compounds as in the present investigation, they provide assurance that the river was well-mixed at this site. In consequence, no further investigation into cross-river variability was undertaken in this study.

SECTION 7 - CONCLUSIONS

The data gathered in this study show very strong temporal variations in the flow of the River Thames and in the concentrations of pesticides, and hence in pesticide loads. A large proportion of the total load over the year was discharged in a comparatively short period of high flows following floods.

The pattern of variation of concentration with time was different for different pesticides. The concentrations of the chlorinated organic pesticides fell after the period of high flow, whilst that for the herbicides seemed to increase, possibly as a result of Spring usage in the catchment.

6.2 METHODS OF ESTIMATING LOAD

As a comparison of methods of estimating loads, this study is a repetition of the earlier one carried out at the same site but for a different group of determinands (Harrison et al 1990). The general conclusion, that methods based on discrete sampling through time suffer from large inaccuracies due to their failure to account fully for variations in concentration and flow, is confirmed. The results of the present study (Table 9) make this point even more forcibly than did the earlier work. Whilst most of the confidence intervals based on Method 2 or 3 do contain the 'correct' Method 1 result, many of the intervals are, from a practical point of view, very wide.

The previous report went to some length to discuss the relative merits of Methods 2 and 3 for treating the grab sample data, but without reaching a firm conclusion. The present study provides no additional information that could help to resolve this point. The very strong temporal variations in flow raise the question whether the formulae for confidence intervals for estimates of load are correct for either Method 2 or Method 3, although the results of the study do not suggest that the widths of these confidence intervals are being over-estimated.

The statistical theory associated with Methods 2 and 3 has previously been based on assumptions that the instantaneous measurements of flow and concentration are taken in a framework of simple random sampling (see Section 5.1). In the previous report (Harrison et al 1990) the validity of this assumption was questioned but accepted as an approximate enough basis on which to build. With a flow pattern such as encountered in 1989/90 it is more difficult to sustain this assumption and so the derivation of the confidence intervals must be regarded as doubtful. This whole question deserves further investigation but there is unlikely to be any easy solution if the assumption of simple random sampling is discarded. This further emphasises the advantage of systems of continuous monitoring, such as the flow-proportional sampler, for which statistical interpretation is much easier.

REFERENCES

HARRISON R M, THOROGOOD G A and LACEY R F (1990) Comparison of load estimation from grab samples and continuous flow-proportional sampling. WRc Report PRS 2383-M.

WALLING D E and WEBB B W (1985) Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Marine Pollution Bulletin, 16(12), 488-492.

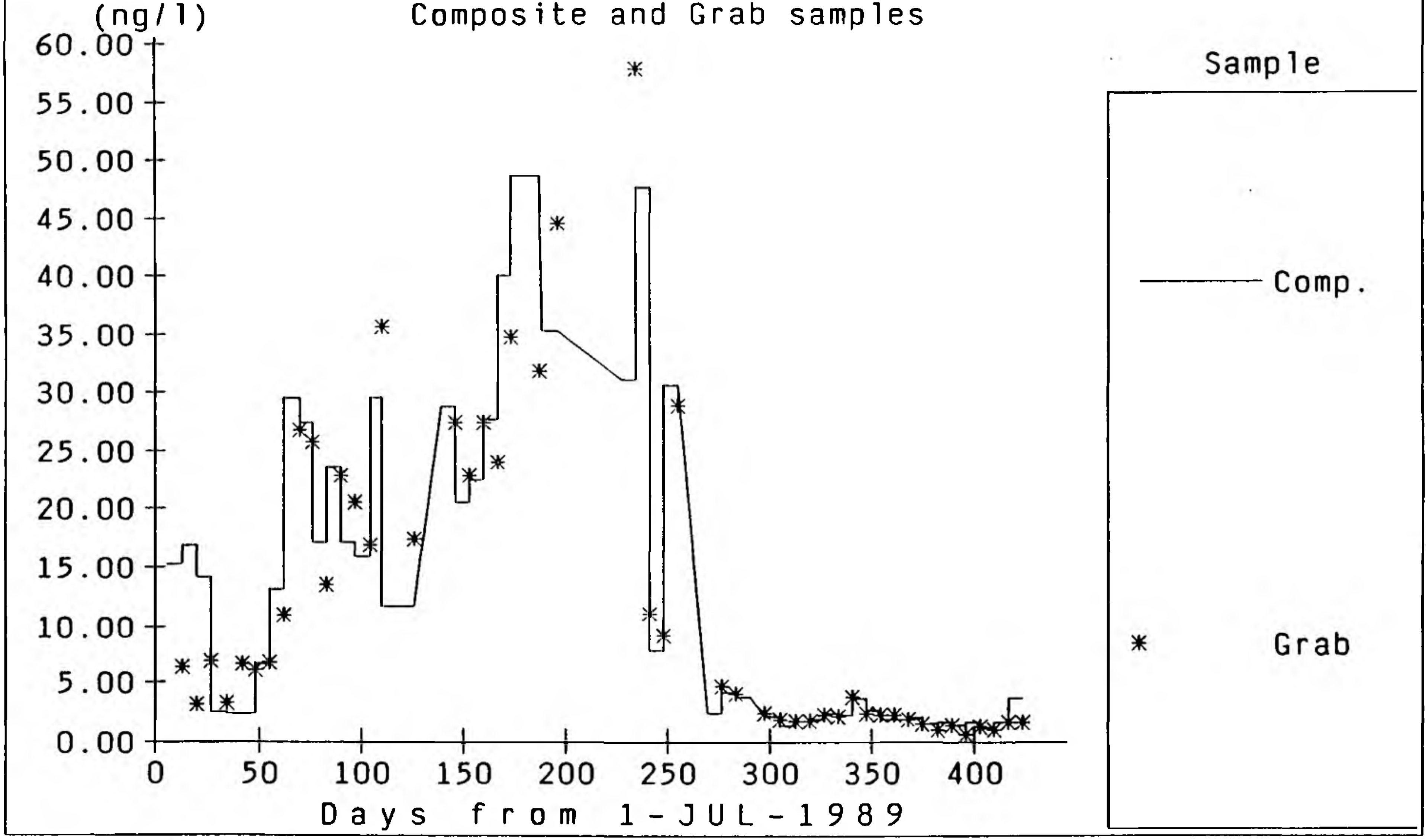
Estimates of annual load based on weekly grab samples could differ from those achieved by continuous flow-proportional sampling by as much as ± 50%. Confidence intervals for estimates of annual load based on grab sampling were often very wide.

This confirms the conclusion of the previous study that methods of load estimation based on discrete sampling through time suffer from large uncertainties due to their failure to account fully for variations in concentration and flow. This is particularly so because of the possibility that peaks can be inadequately represented or completely missed.

ACKNOWLEDGEMENTS

The University of Essex and WRc thank the National Rivers Authority Thames Region for its help and facilities made available for this research.

Figure 2.1 Lindane - Concentration in Composite and Grab samples



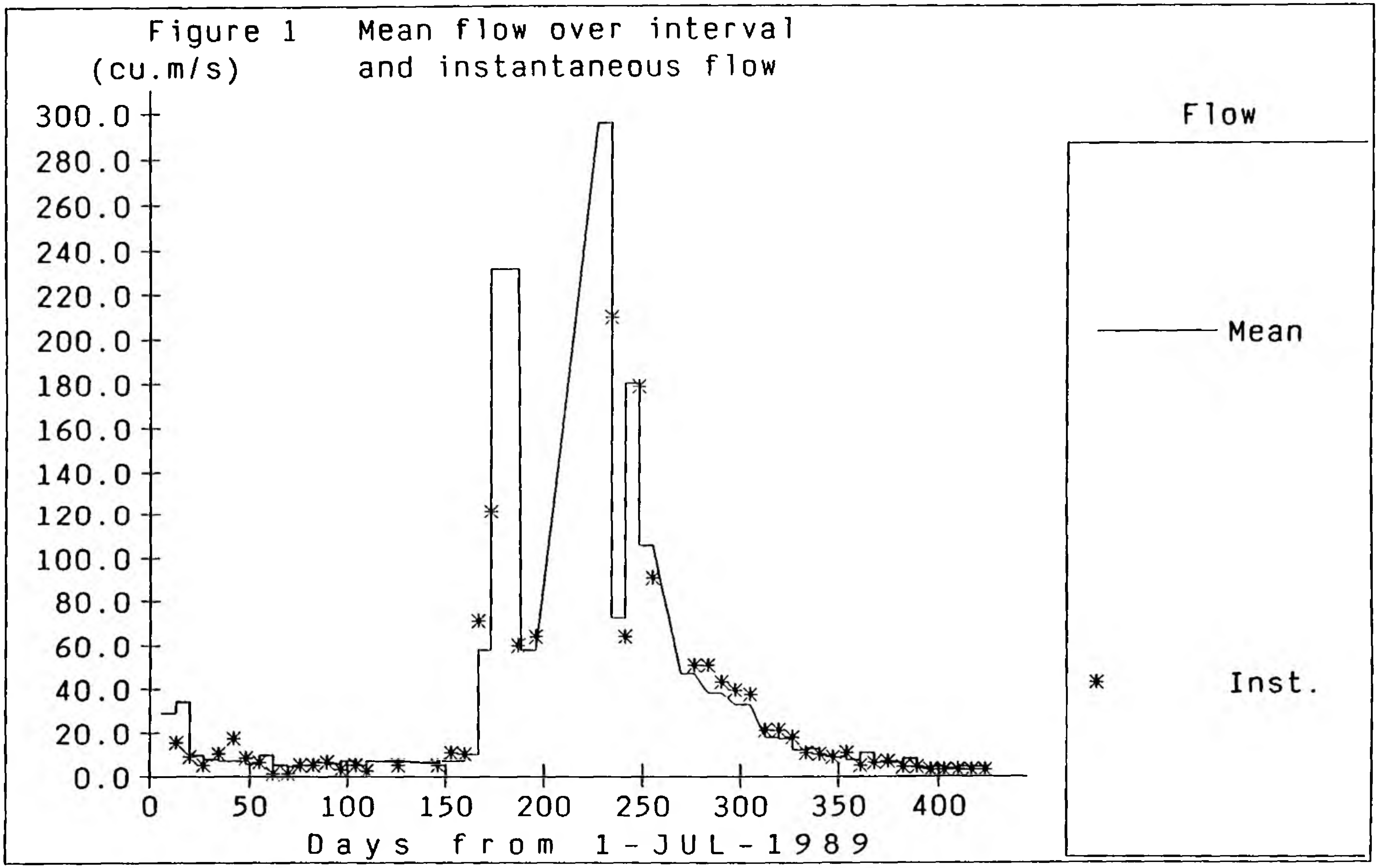


Figure 1 Mean flow over interval and instantaneous flow

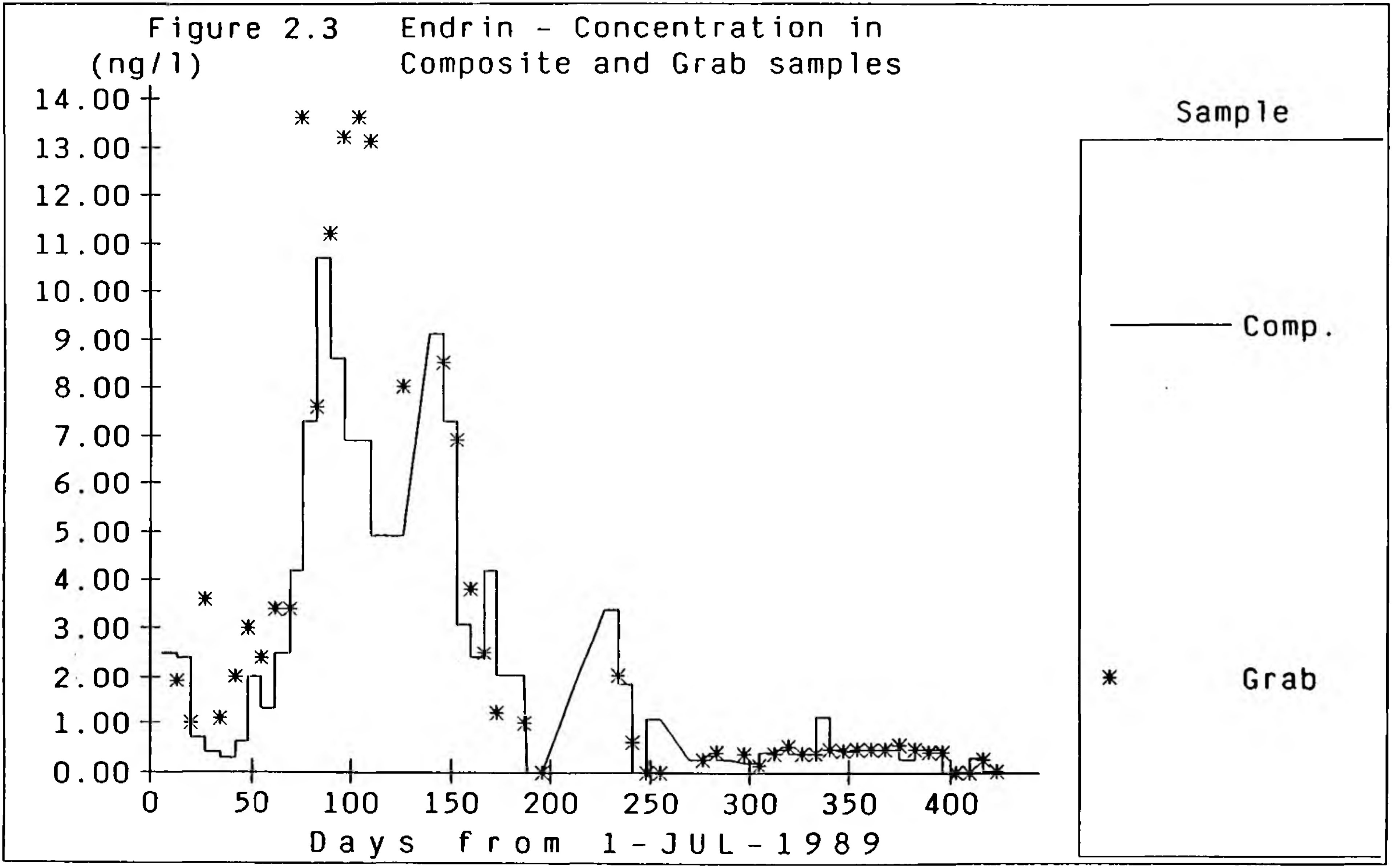


Figure 2.3 Endrin - Concentration in Composite and Grab samples

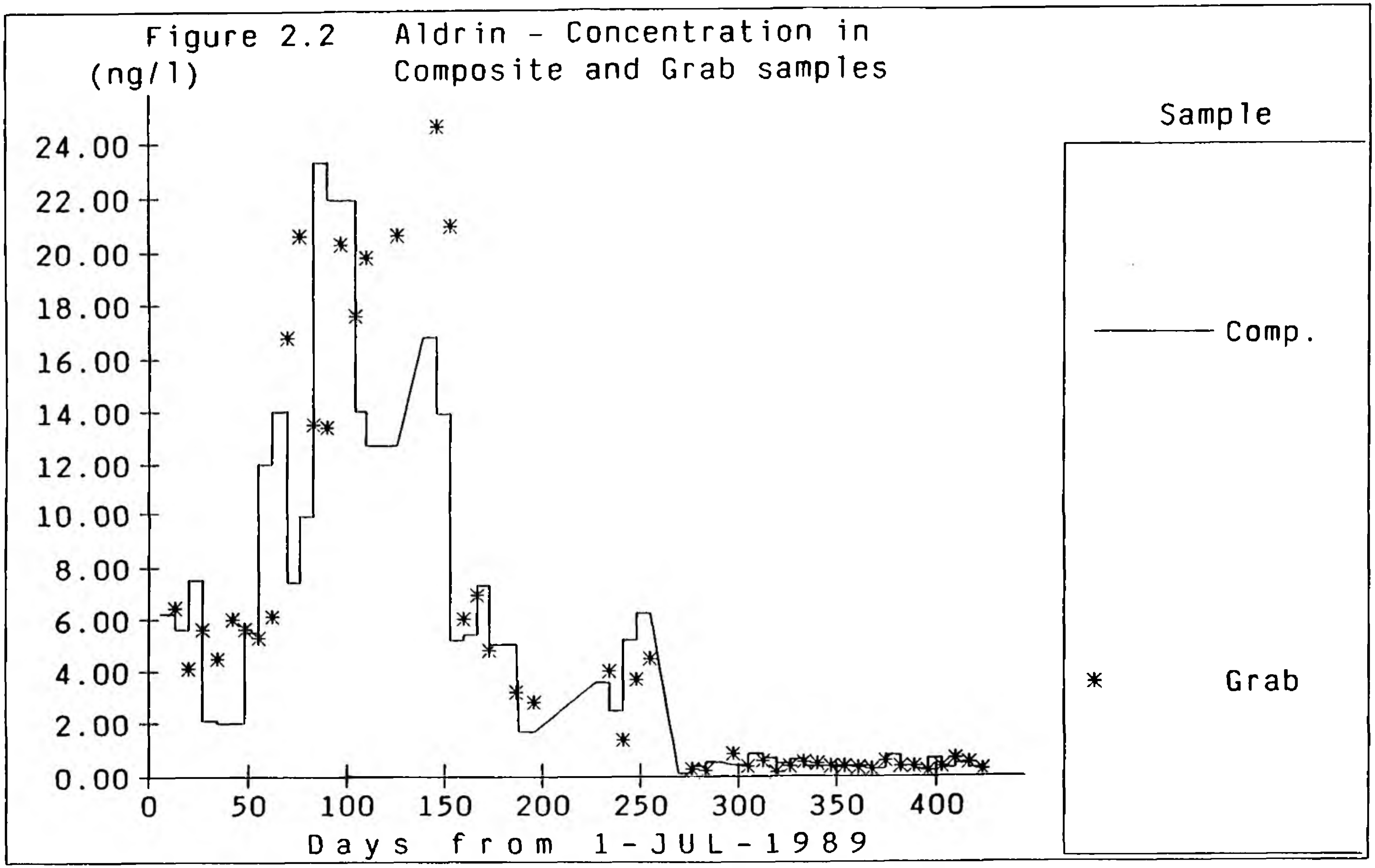


Figure 2.2 Aldrin - Concentration in Composite and Grab samples

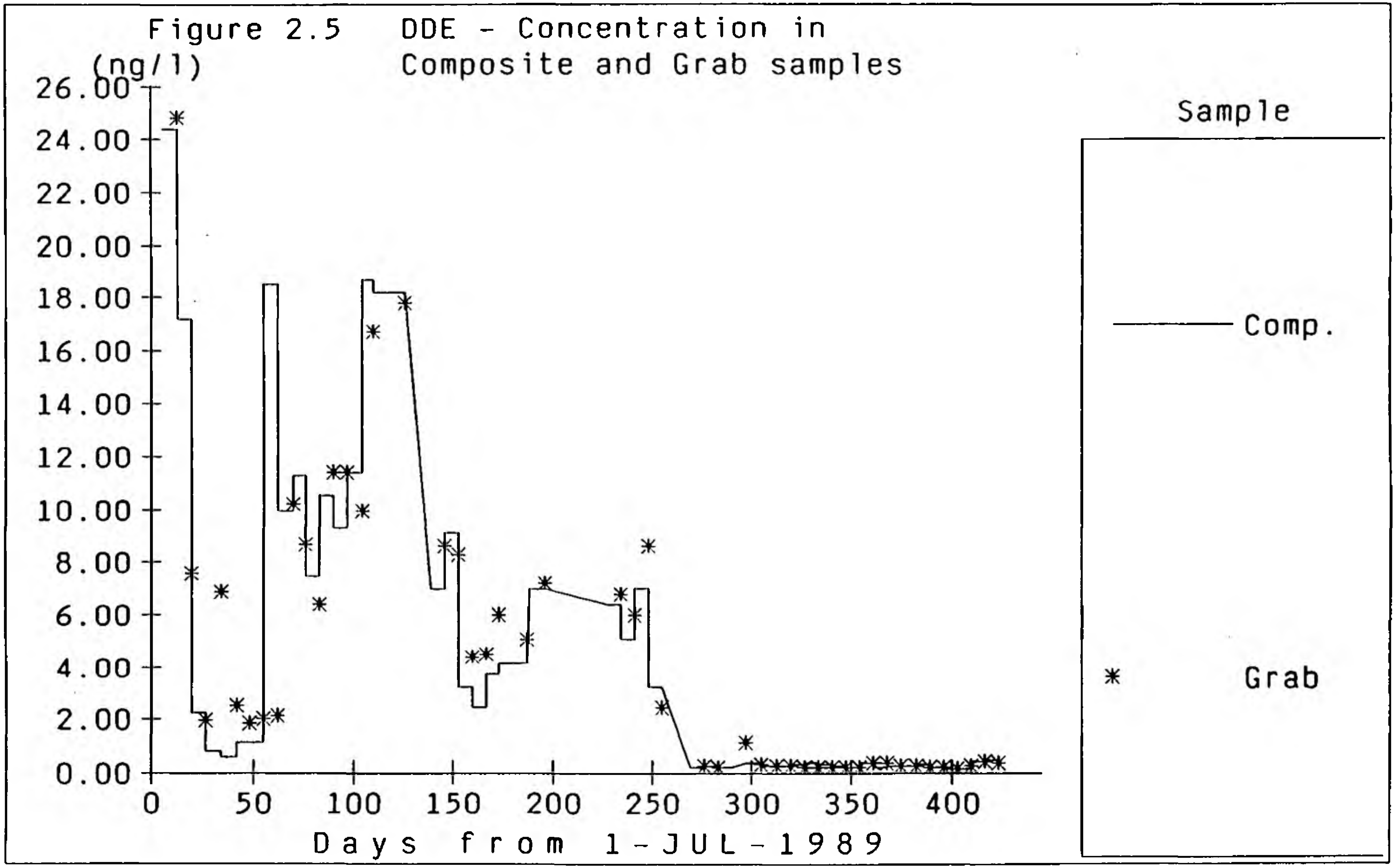


Figure 2.5 DDE - Concentration in Composite and Grab samples

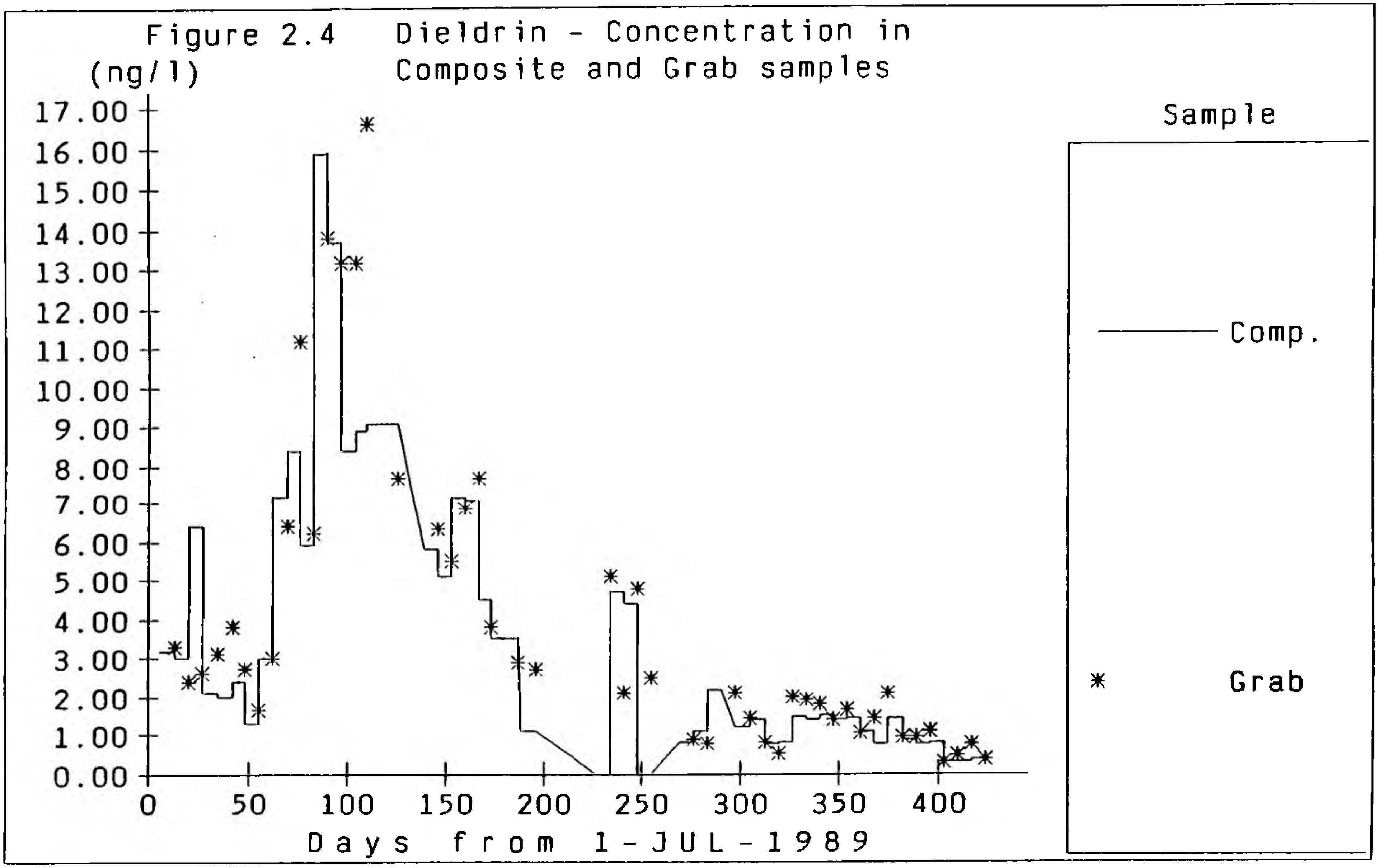


Figure 2.4 Dieldrin - Concentration in Composite and Grab samples

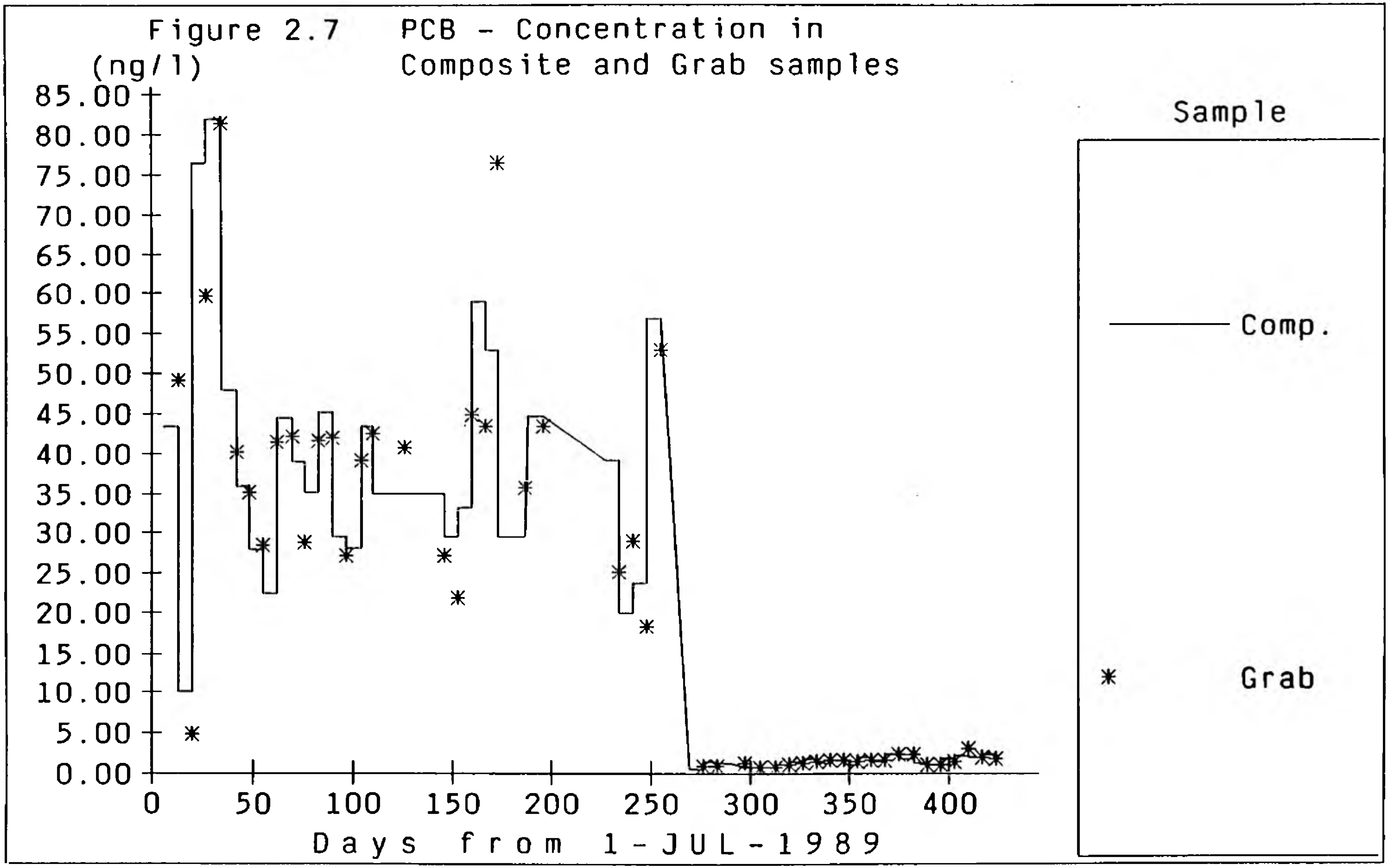


Figure 2.7 PCB - Concentration in Composite and Grab samples

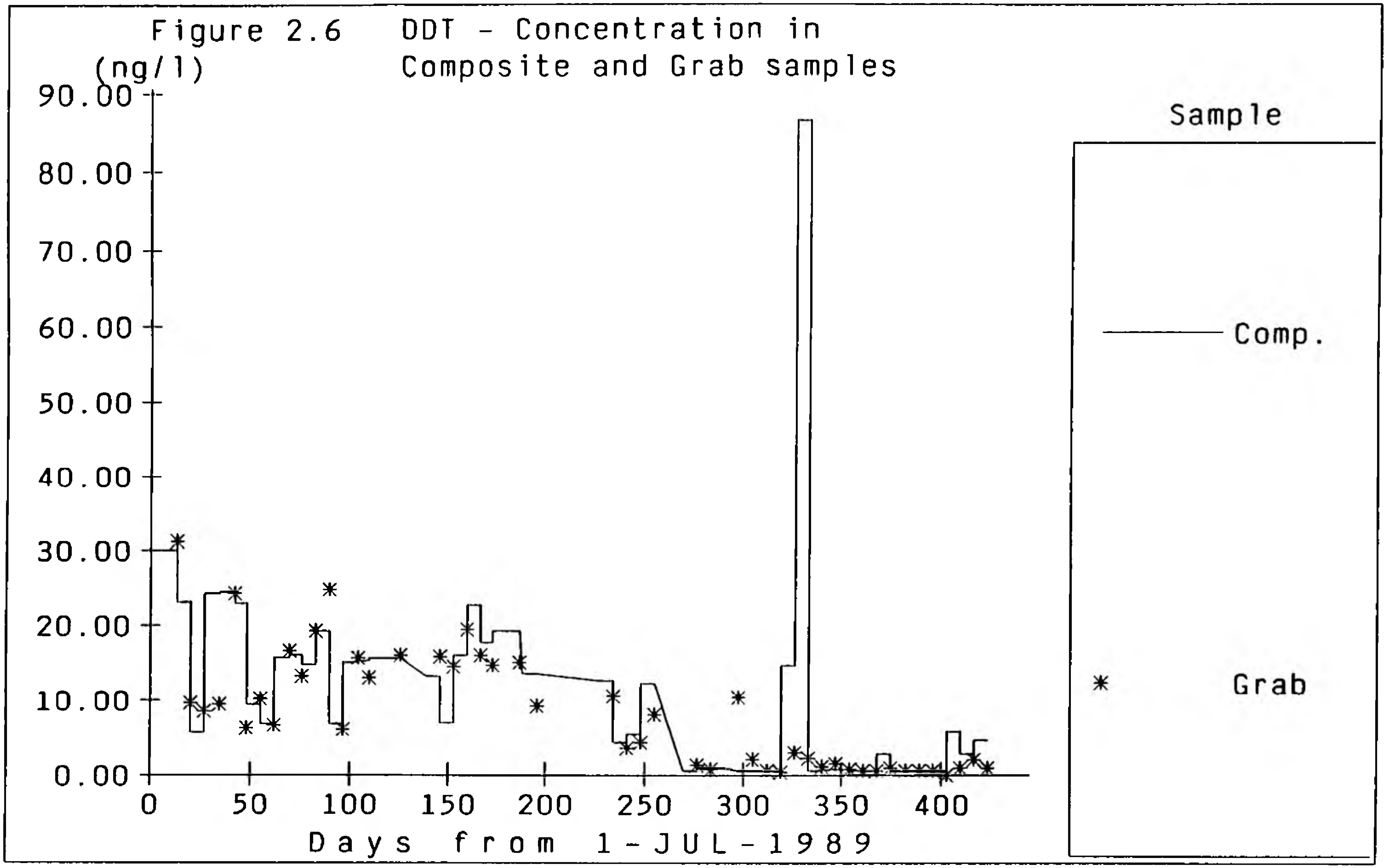


Figure 2.6 DDT - Concentration in Composite and Grab samples

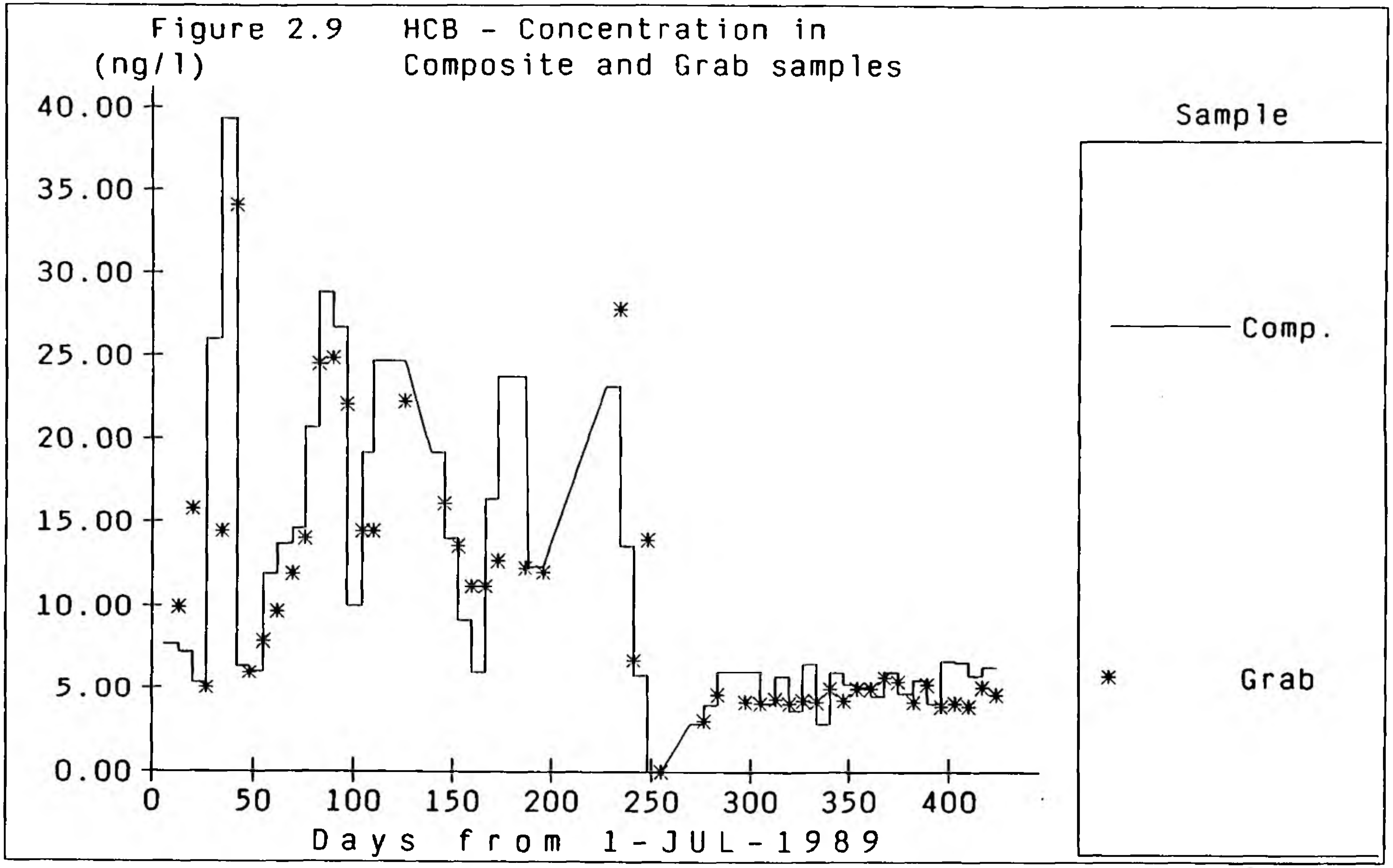


Figure 2.9 HCB - Concentration in Composite and Grab samples

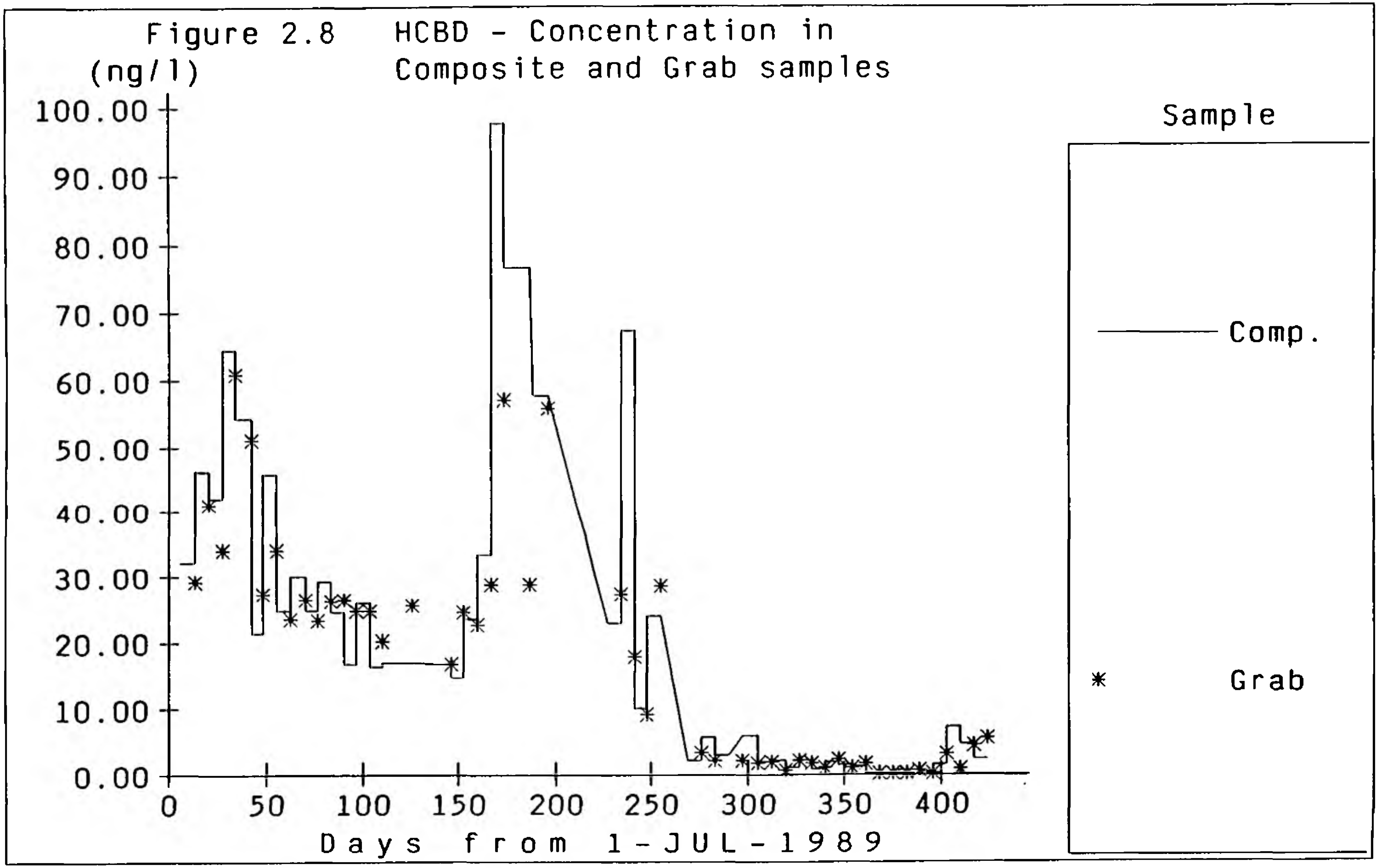
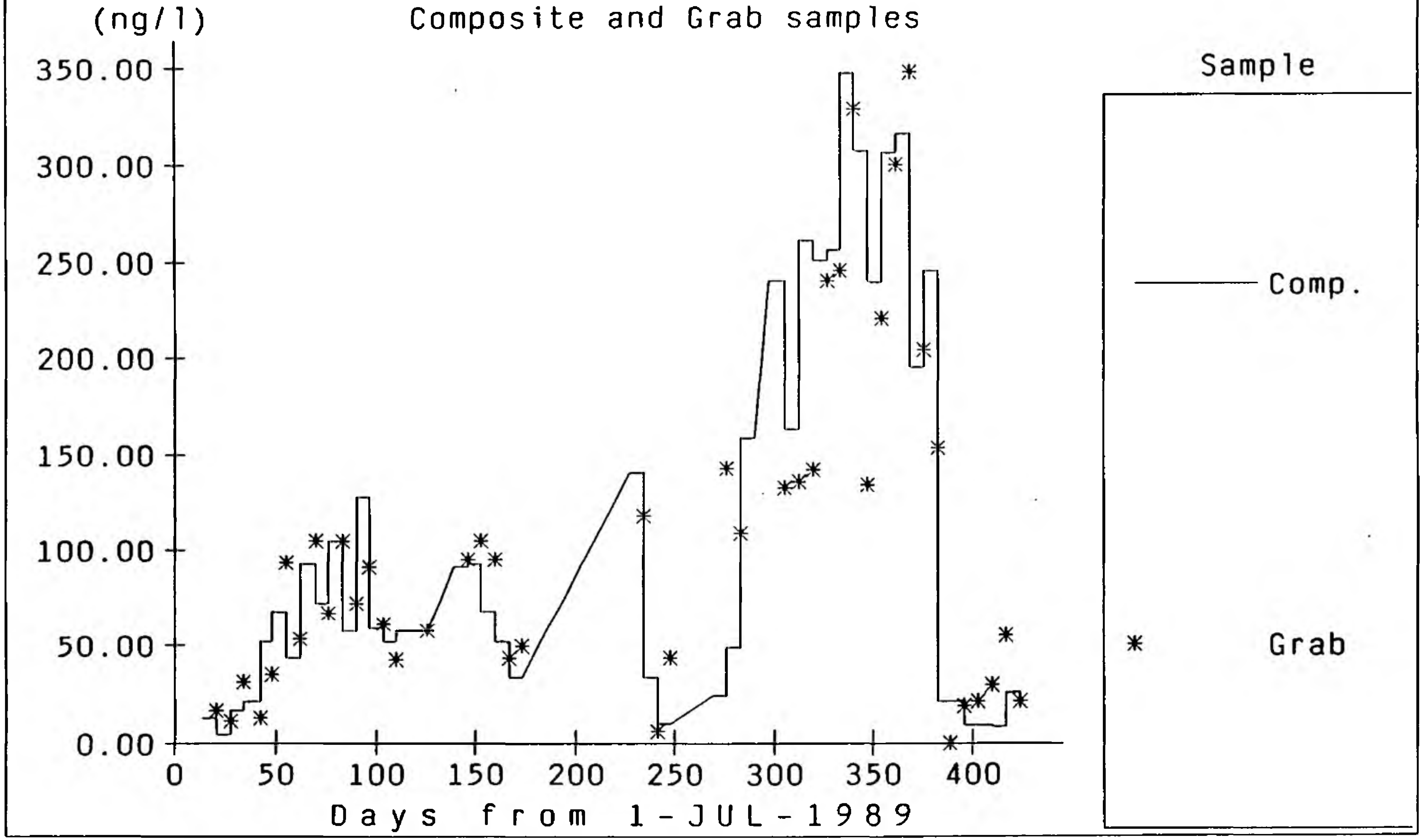


Figure 2.8 HCBD - Concentration in Composite and Grab samples

Figure 2.11 Atrazine - Concentration in Composite and Grab samples



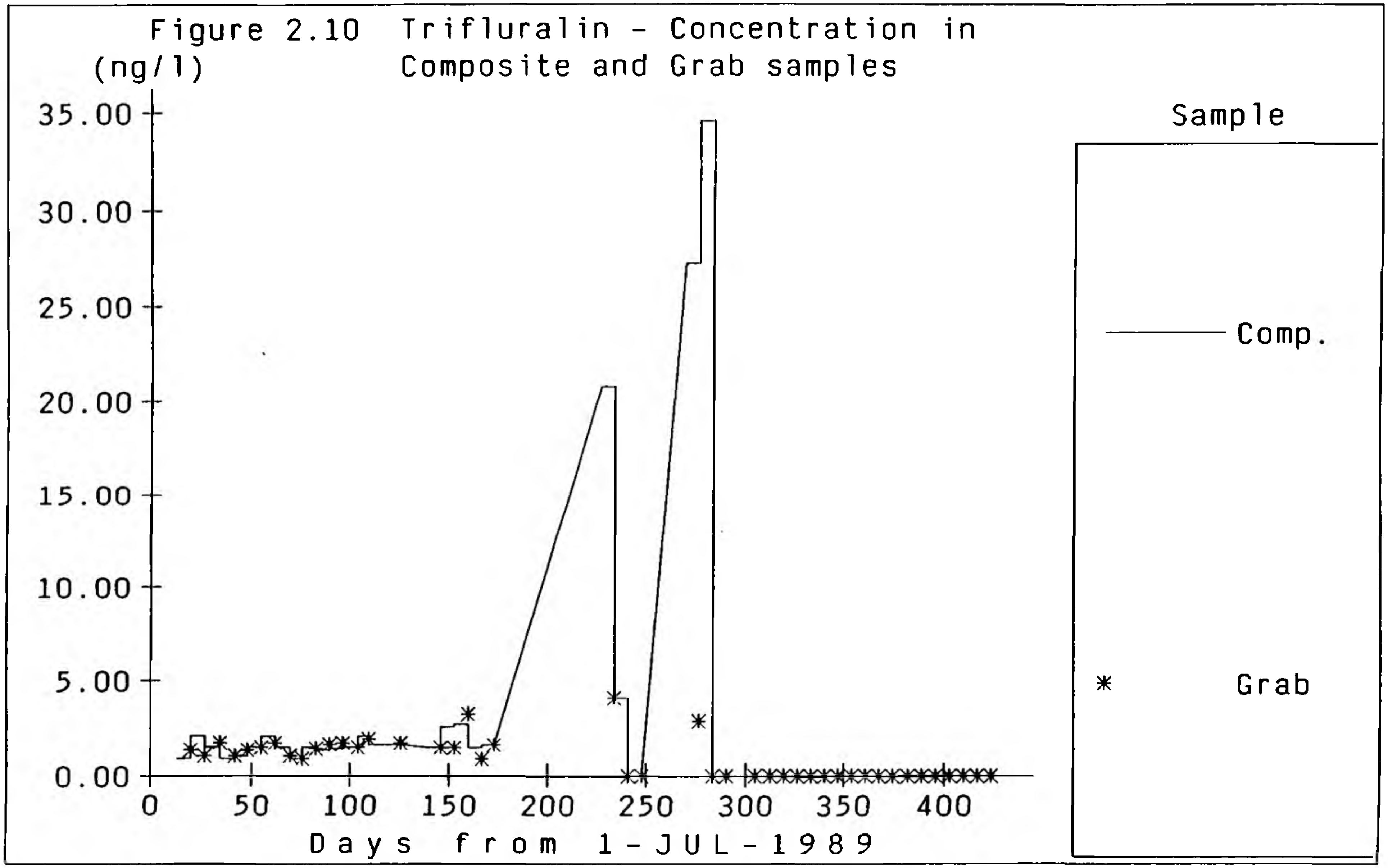


Figure 2.10 Trifluralin - Concentration in Composite and Grab samples

Figure 3.1 Lindane - Concentration against Flow

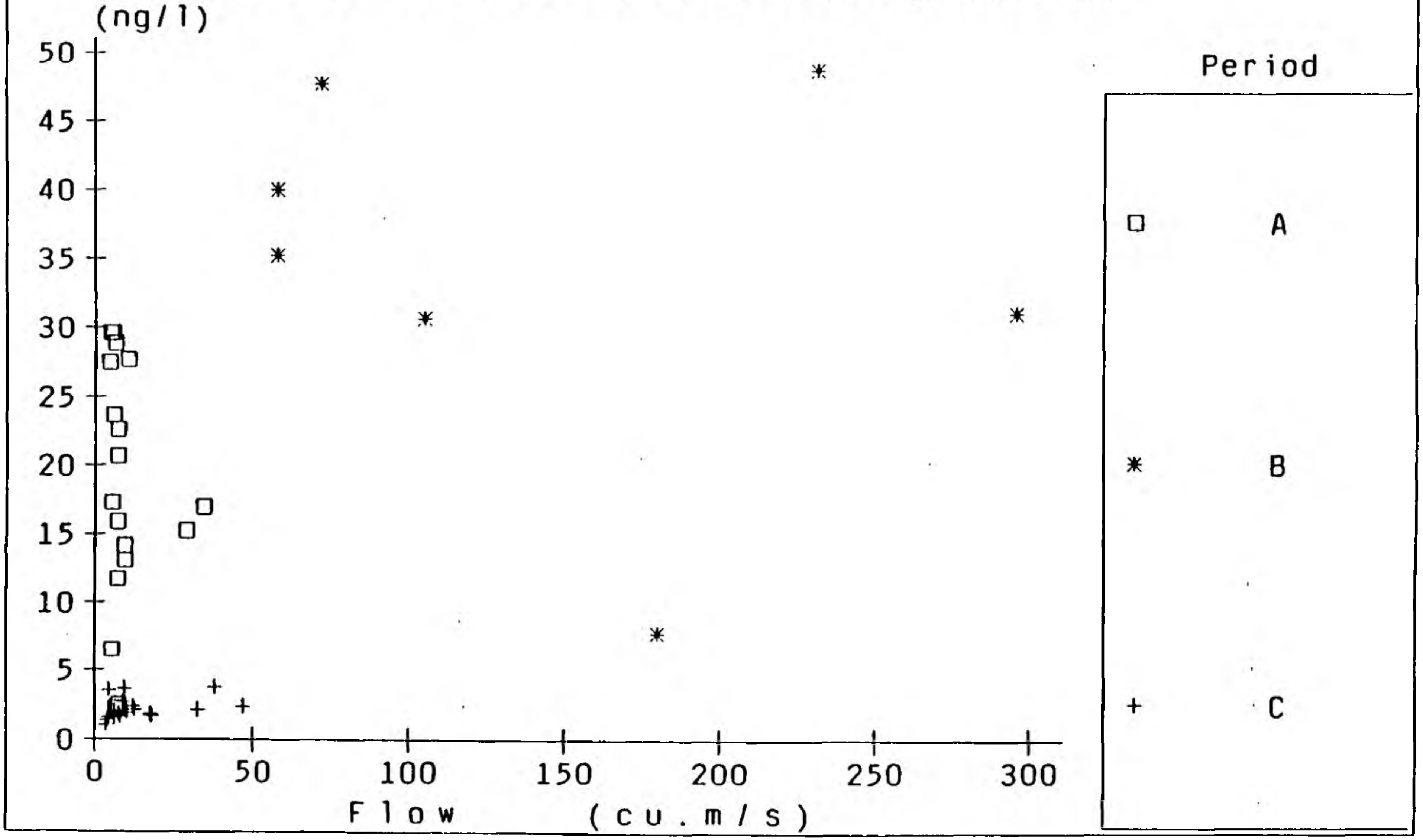


Figure 2.12 Simazine - Concentration in Composite and Grab samples

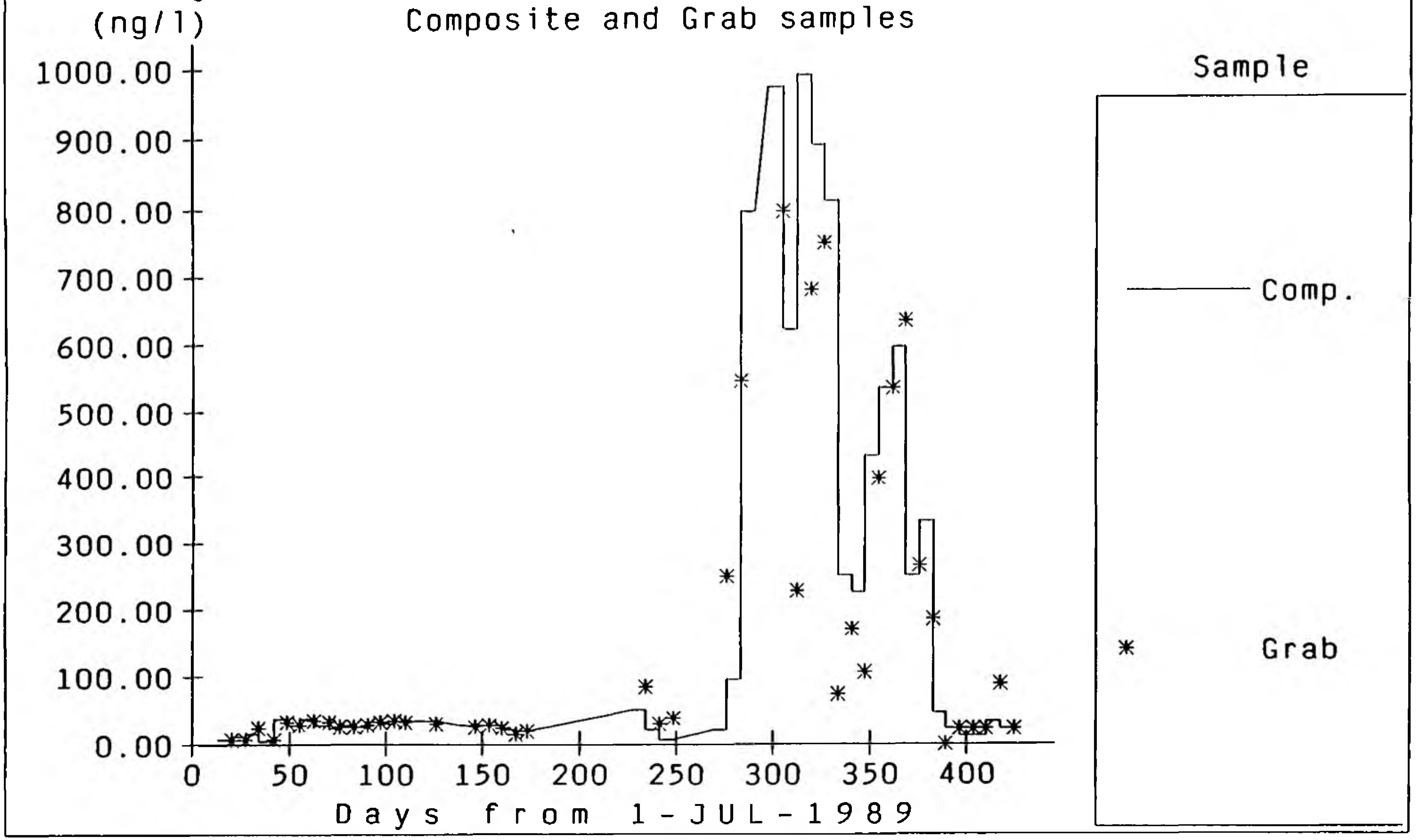


Figure 3.3 Endrin - Concentration against Flow

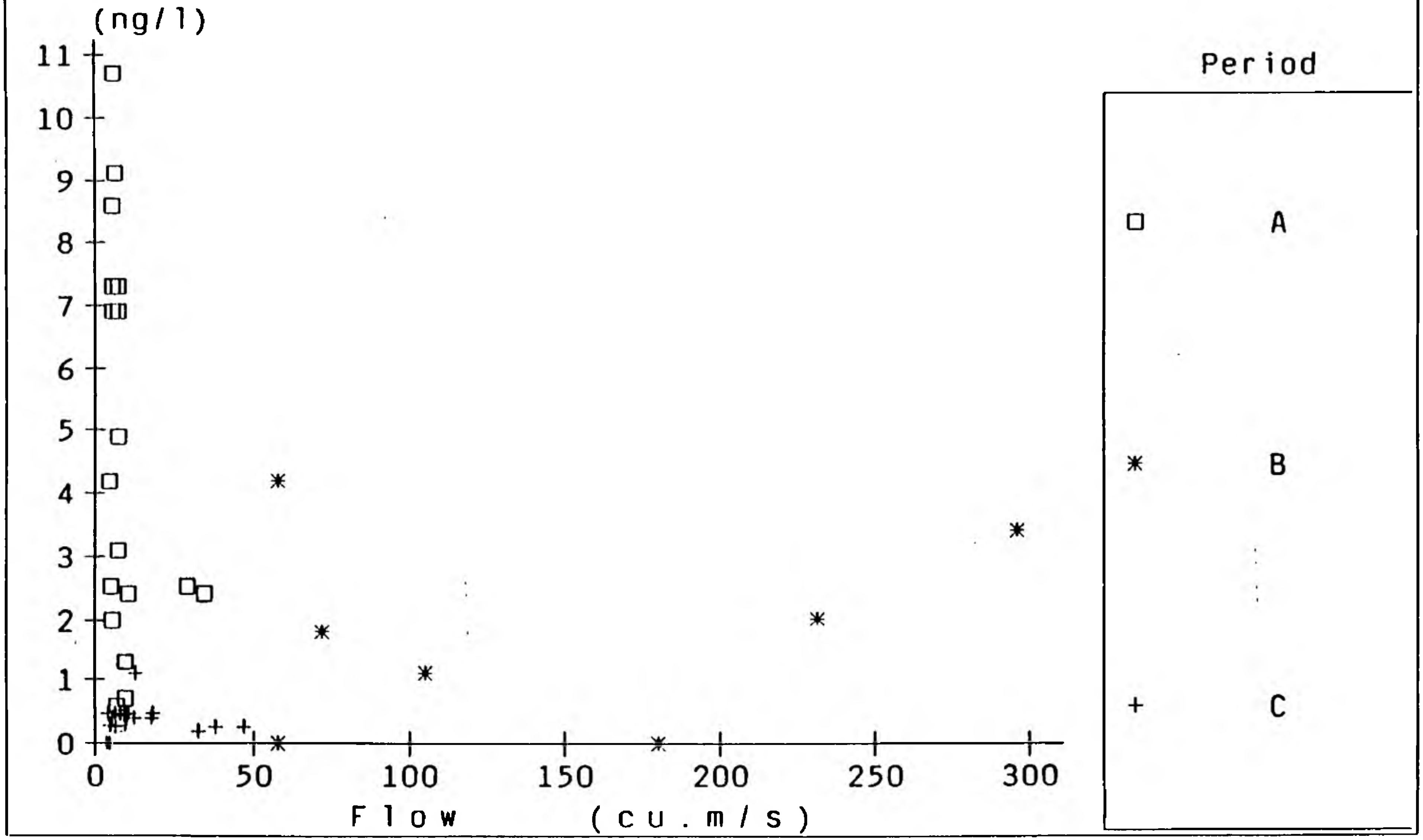
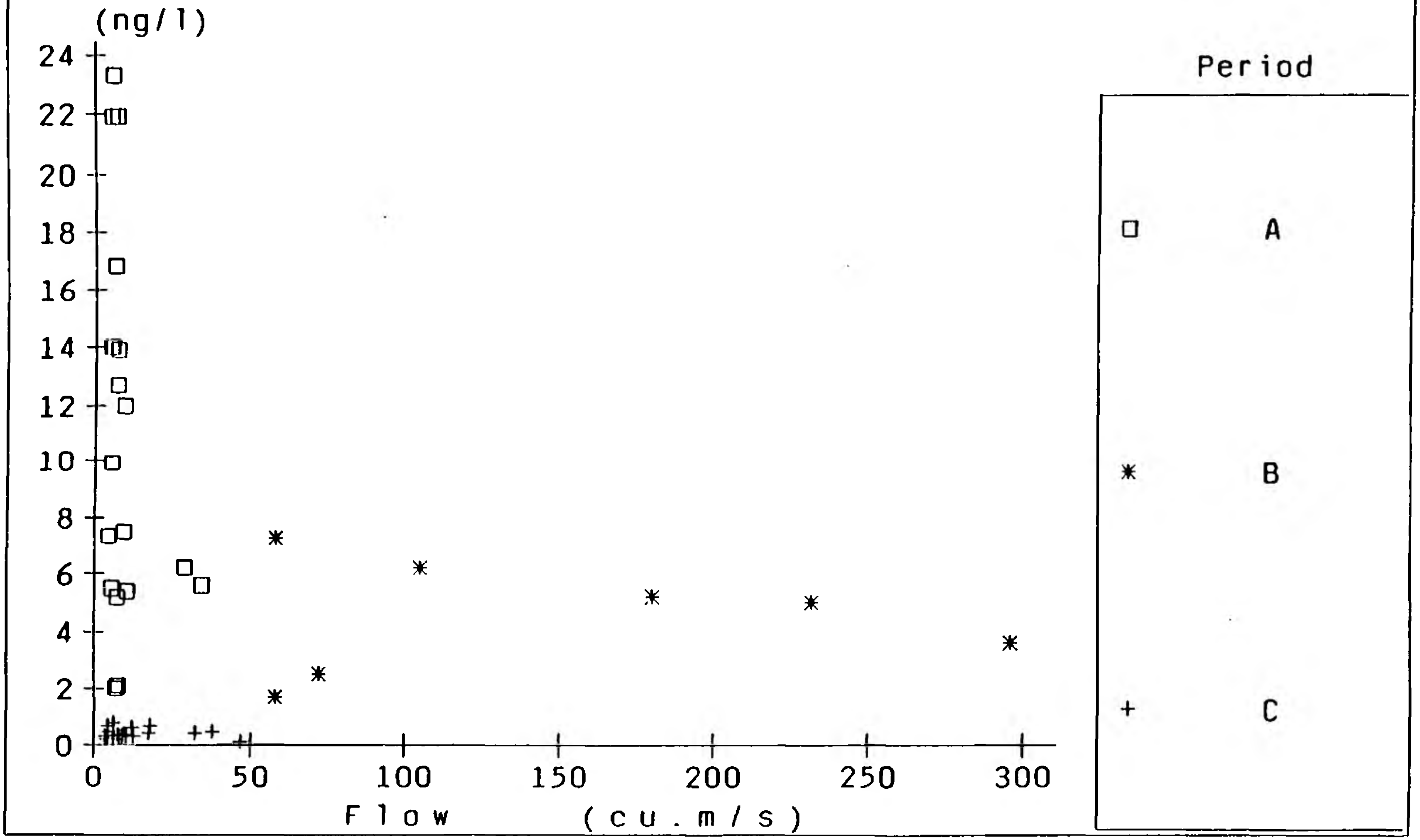


Figure 3.2 Aldrin - Concentration against Flow



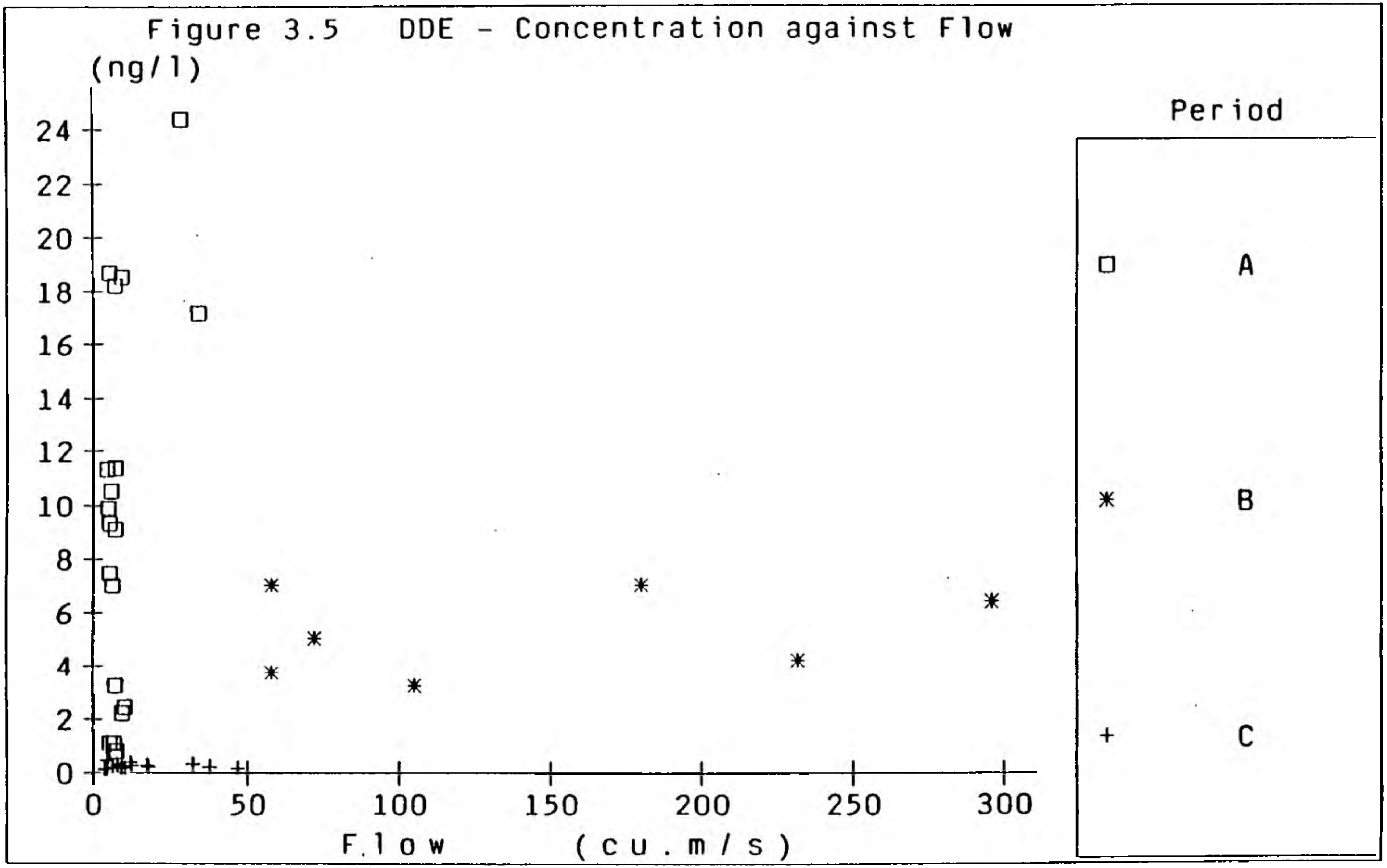


Figure 3.5 DDE - Concentration against Flow

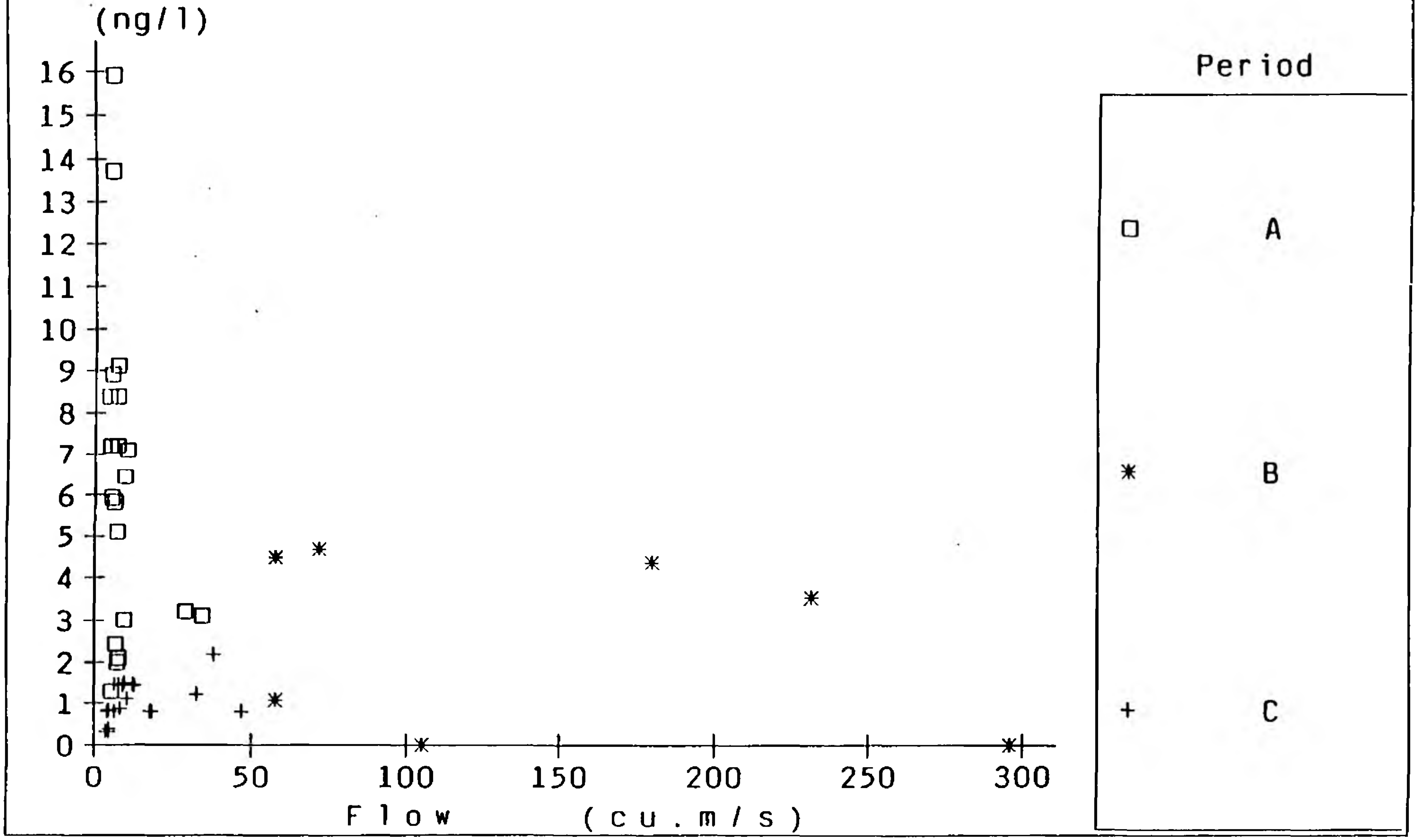


Figure 3.4 Dieldrin - Concentration against Flow

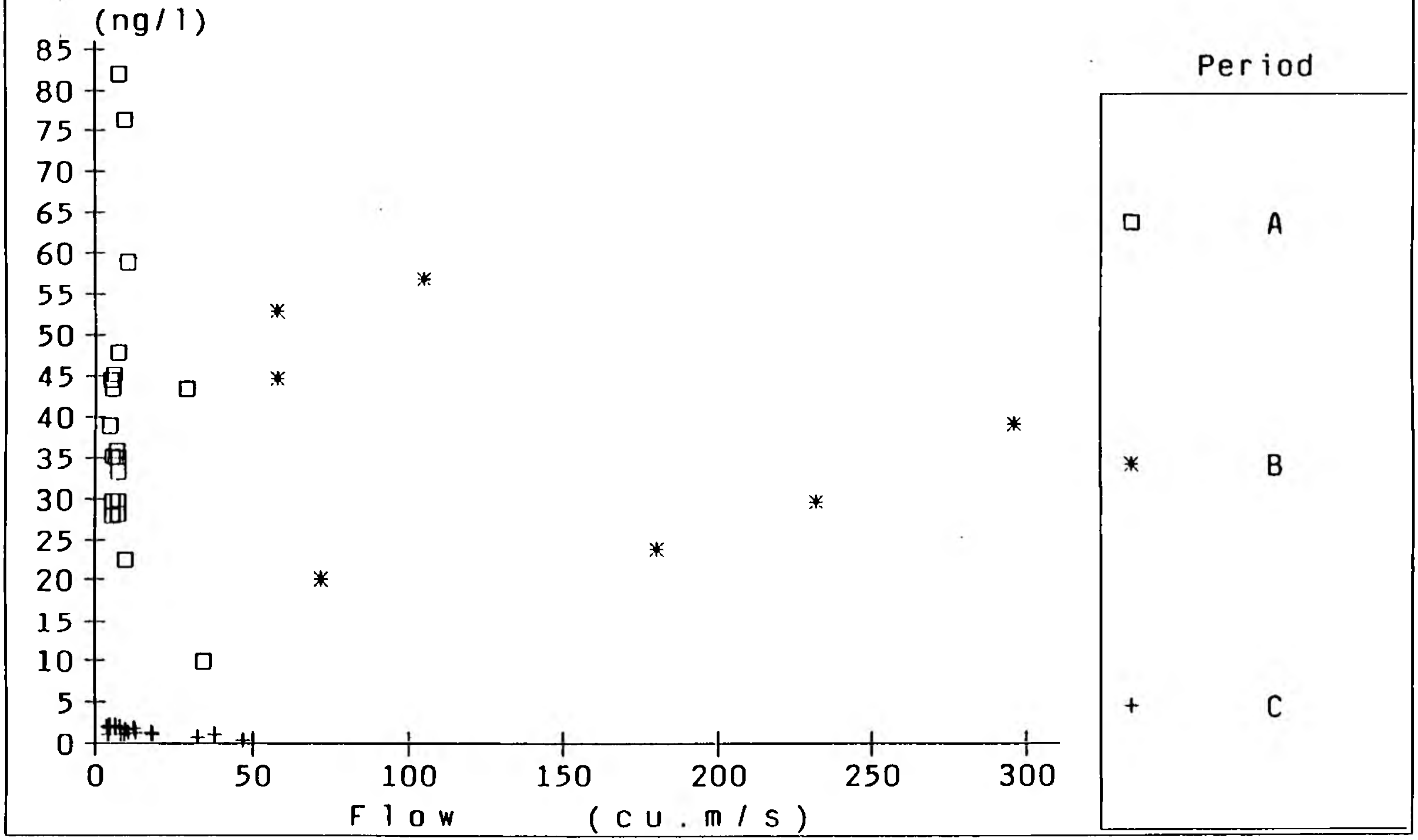


Figure 3.7 PCB - Concentration against Flow

Figure 3.6 DDT - Concentration against Flow

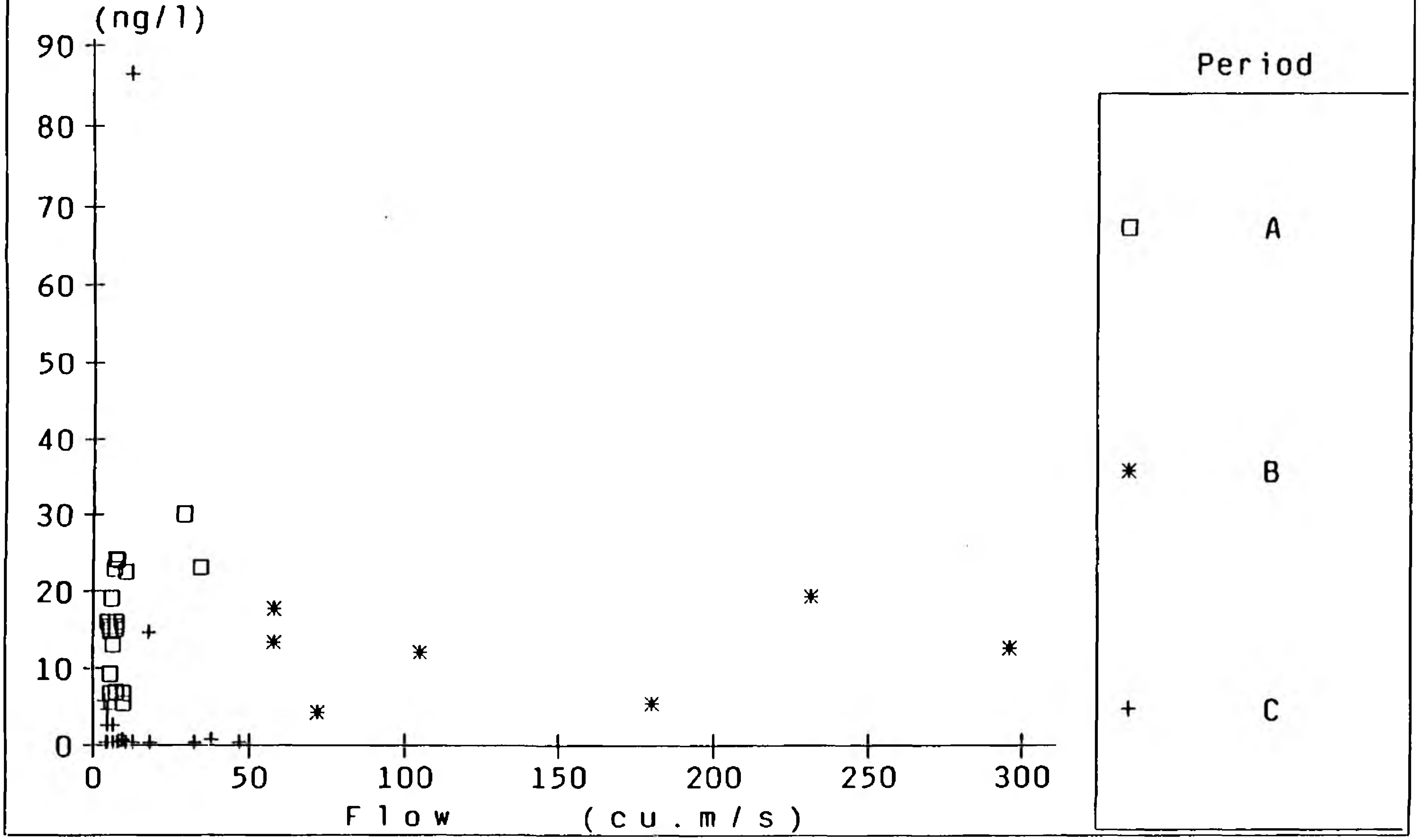
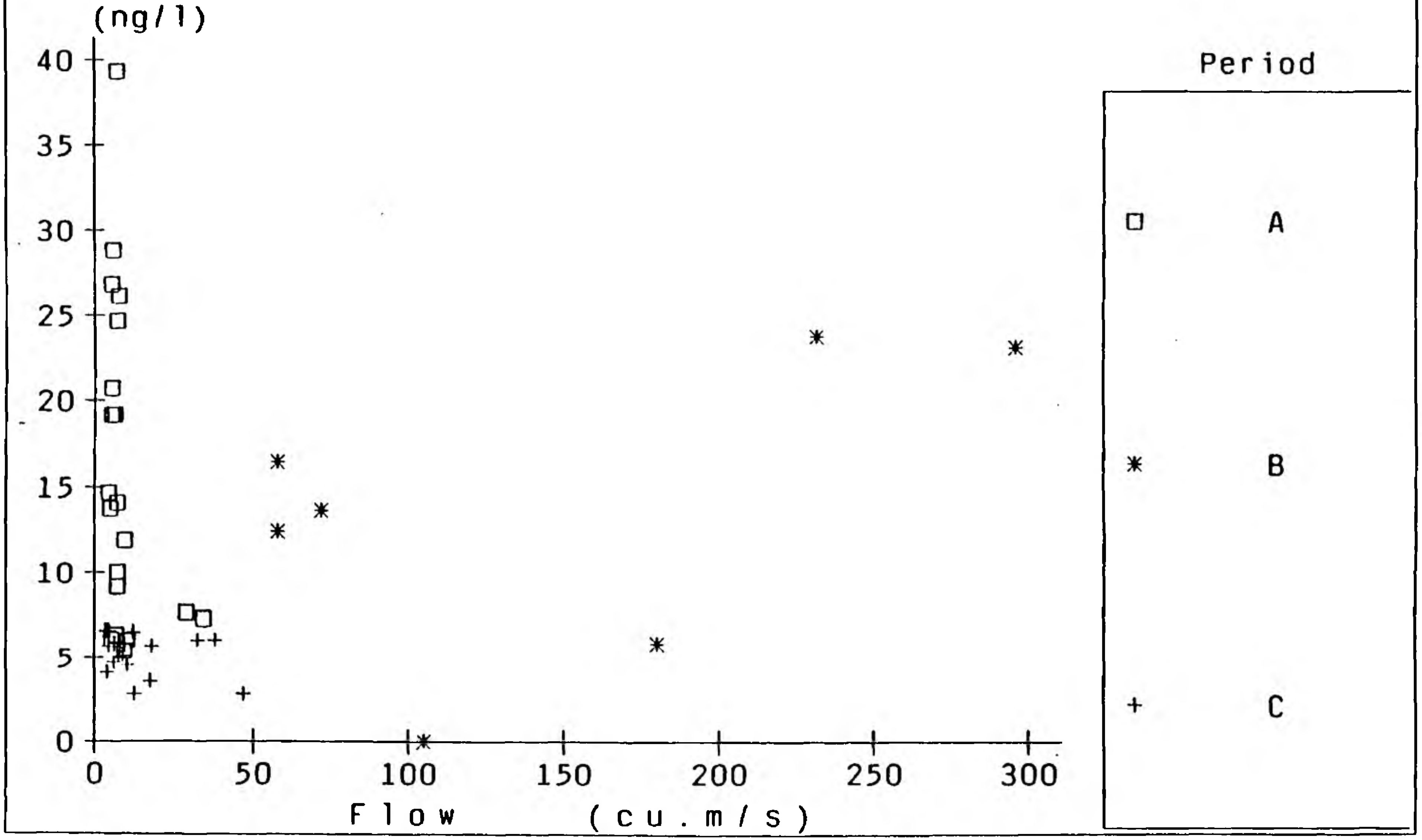


Figure 3.9 HCB - Concentration against Flow



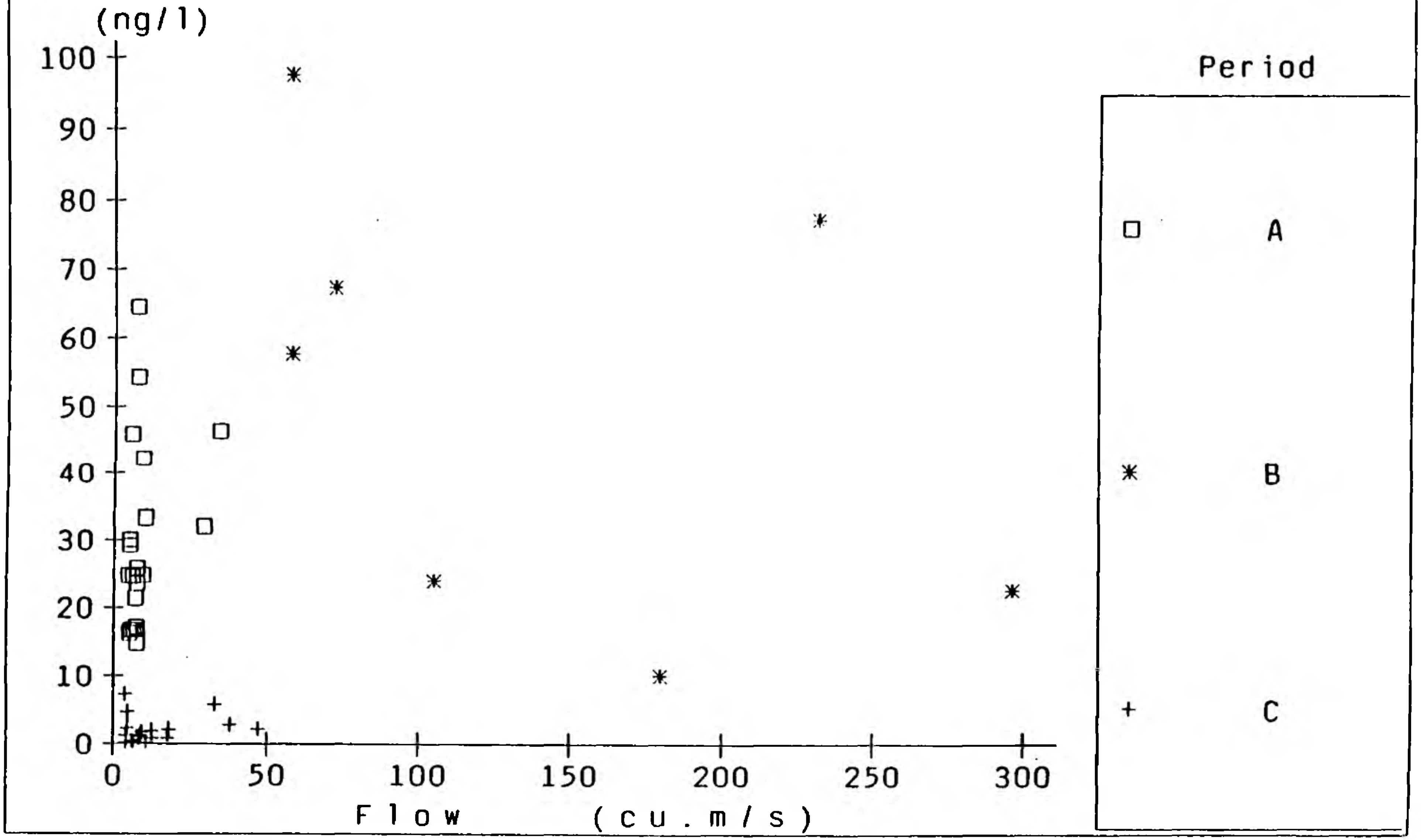


Figure 3.8 HCBD - Concentration against Flow

Figure 3.11 Atrazine - Concentration against Flow

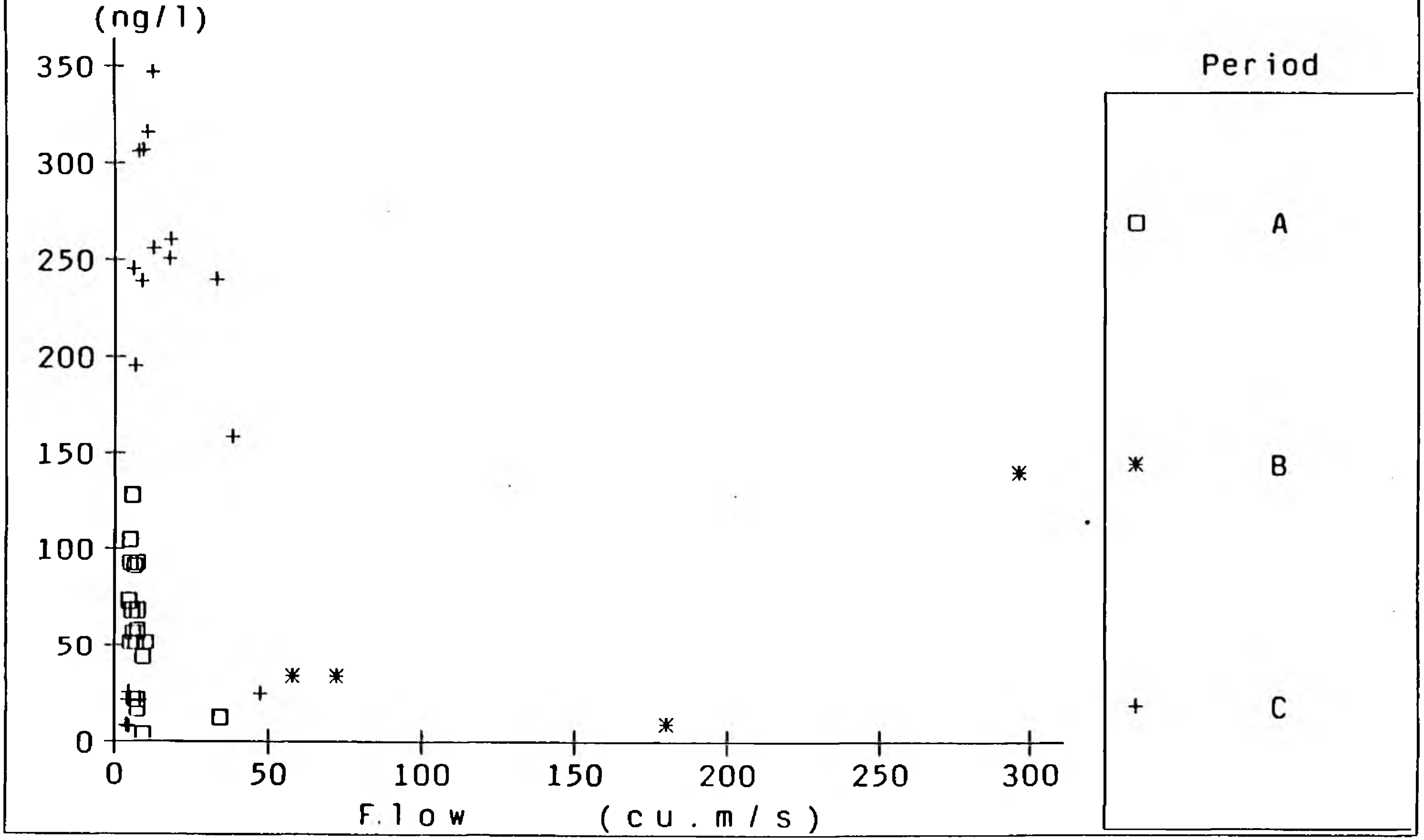
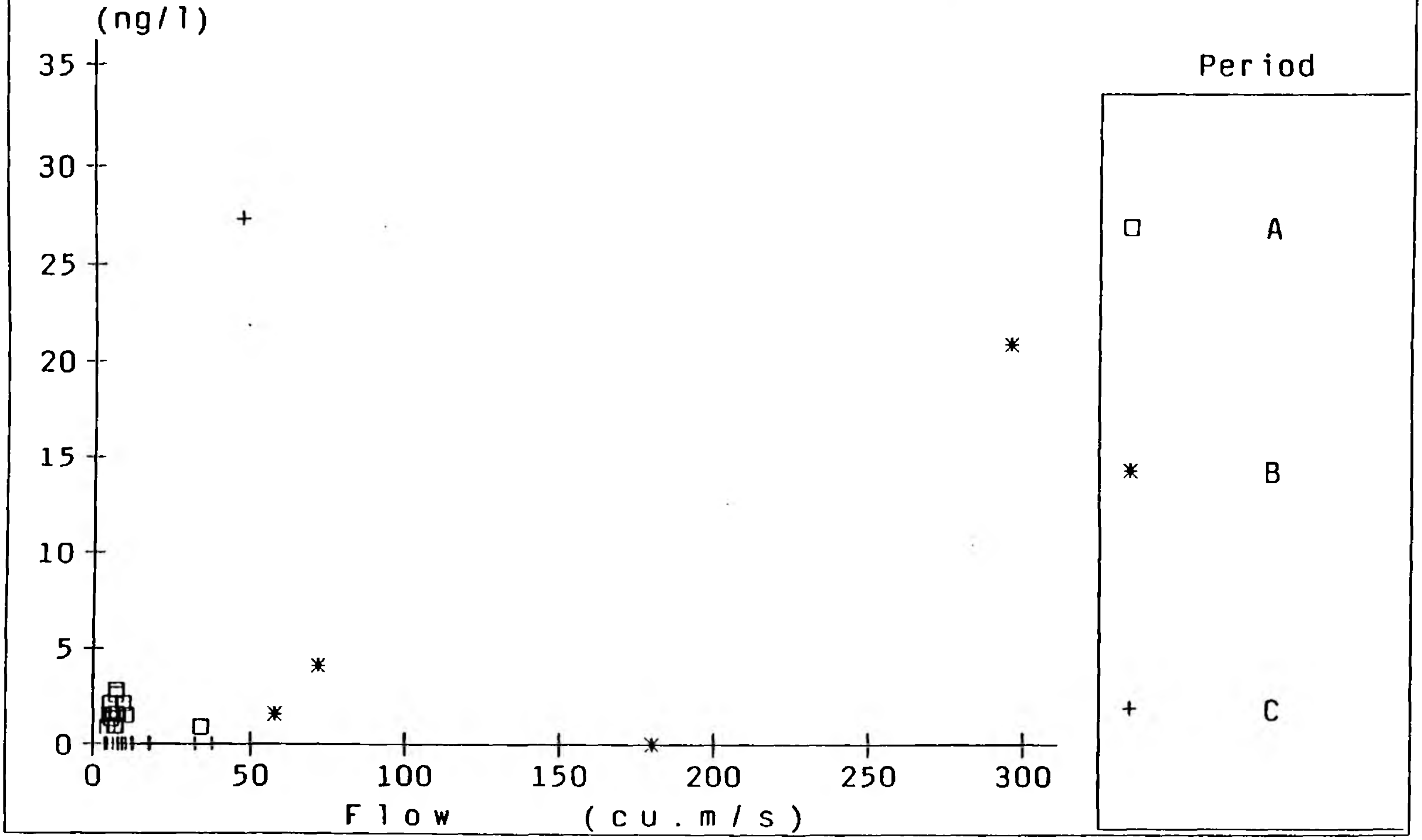


Figure 3.10 Trifluralin - Concentration against Flow



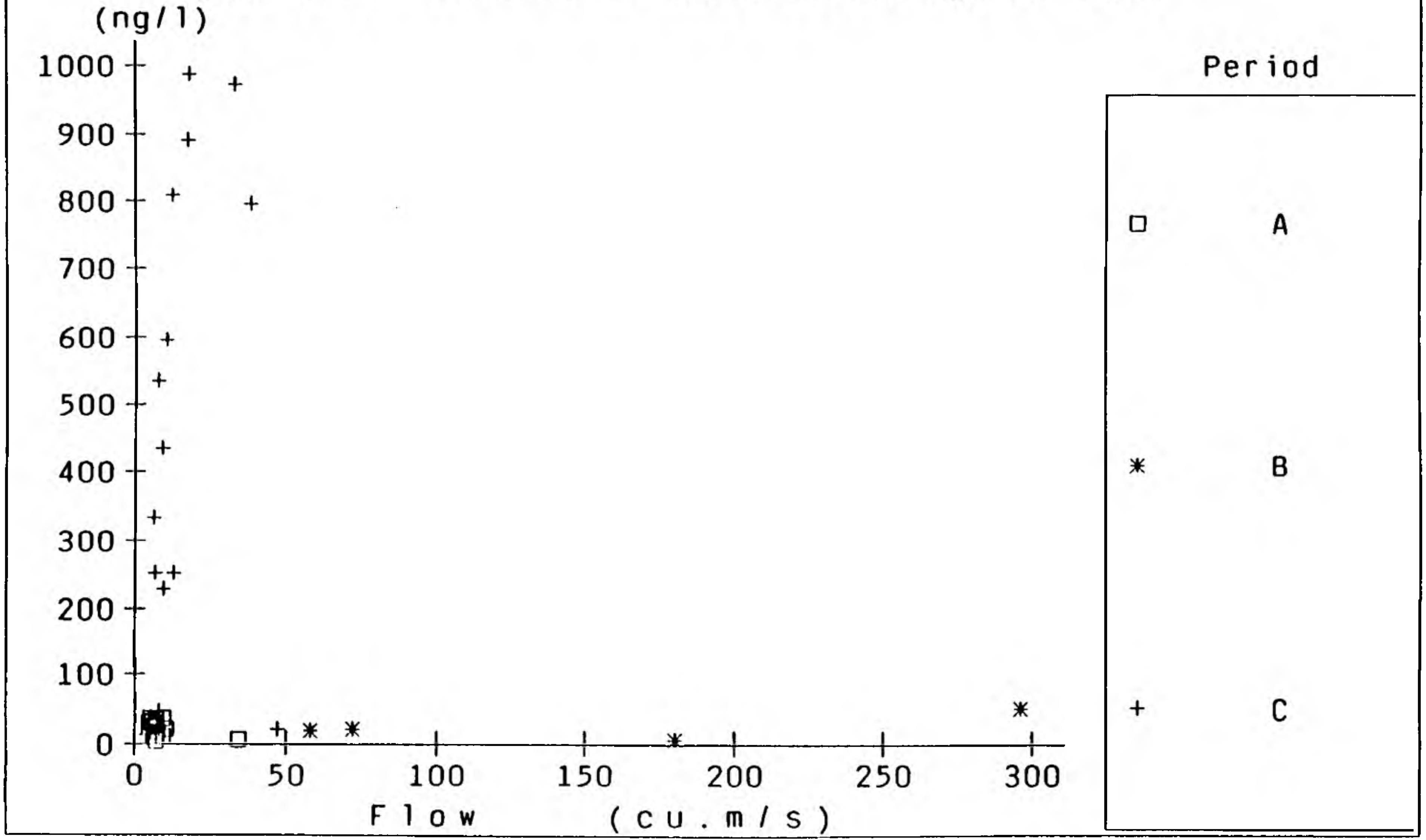


Figure 3.12 Simazine - Concentration against Flow

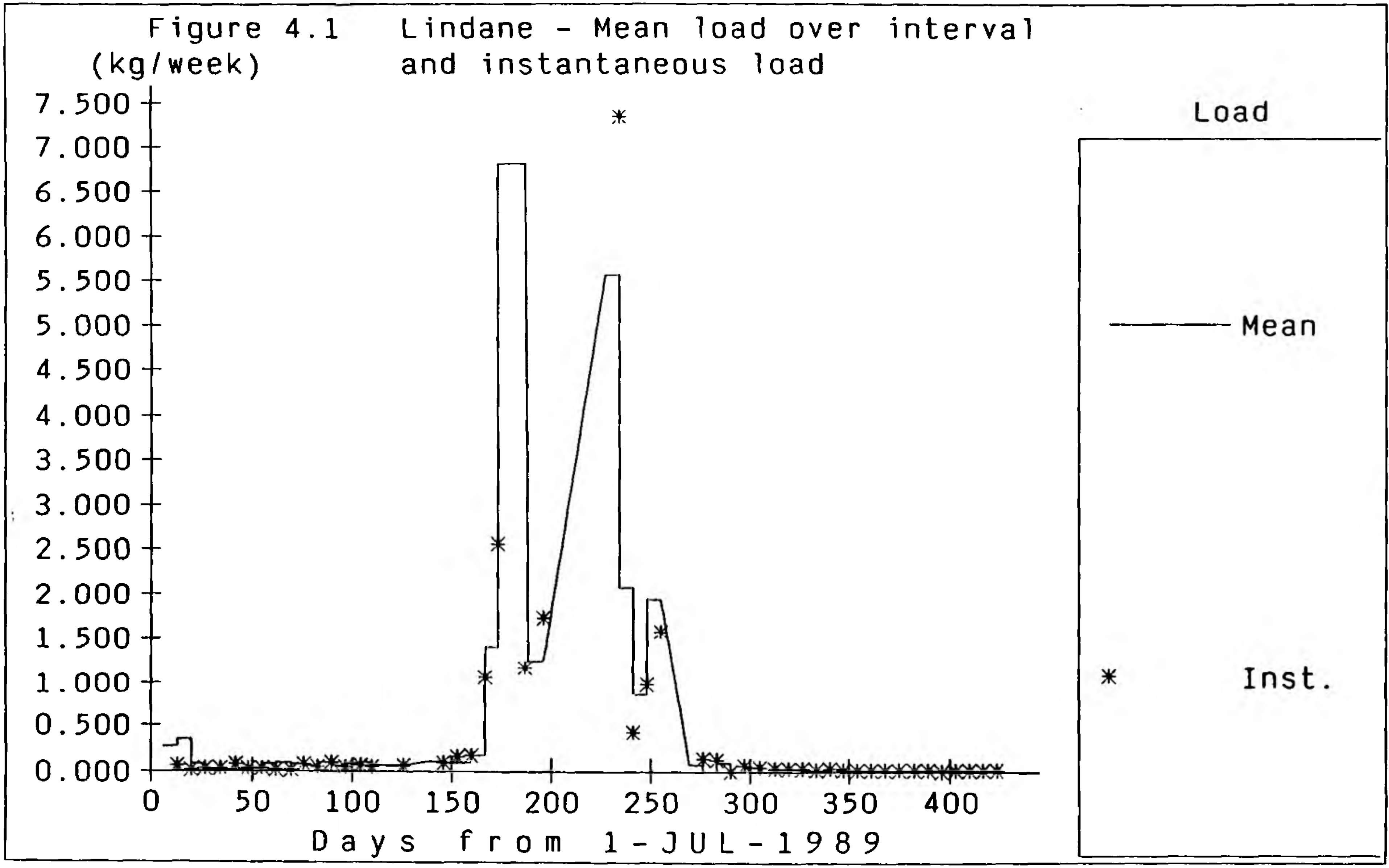


Figure 4.1 Lindane - Mean load over interval and instantaneous load

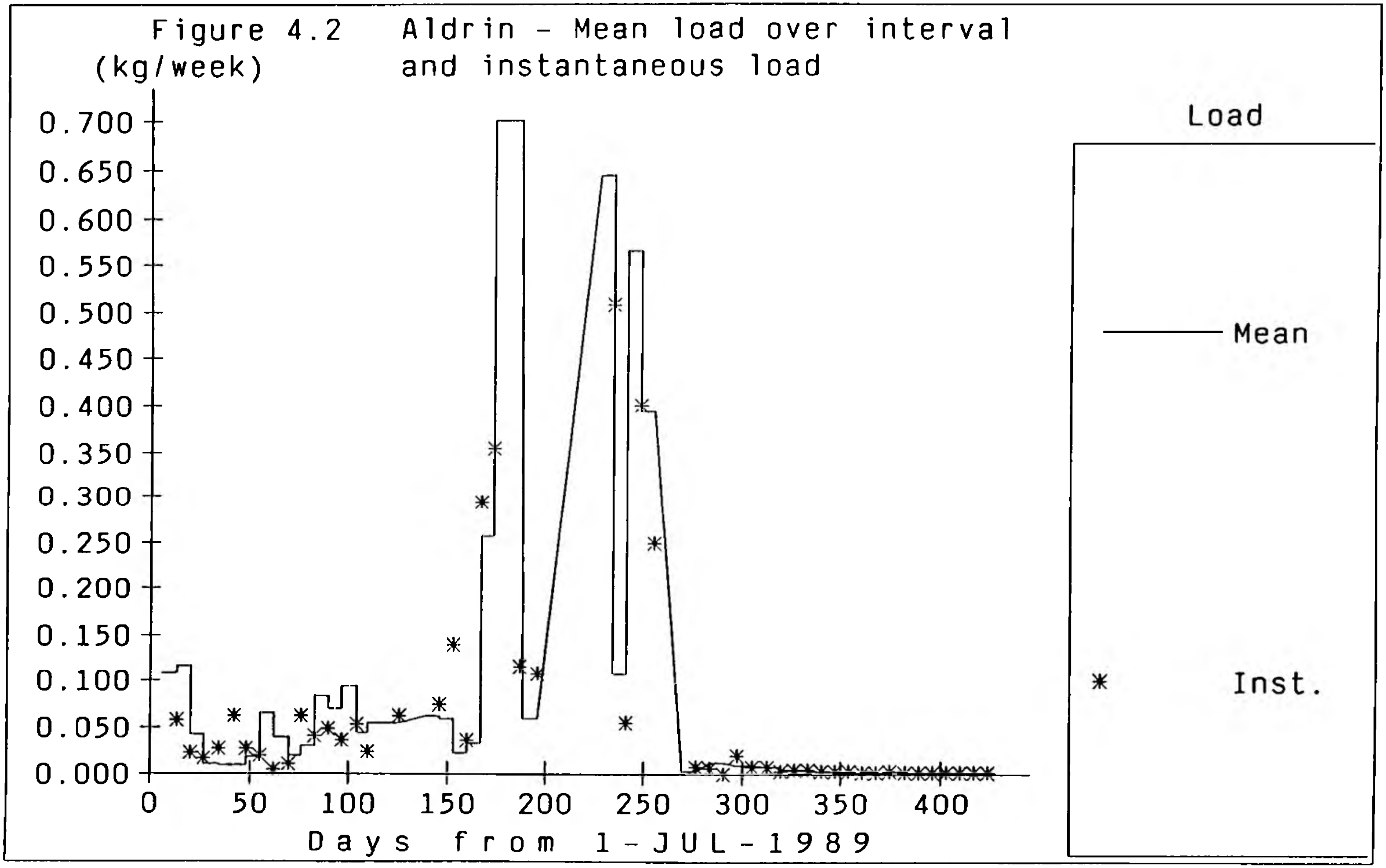


Figure 4.2 Aldrin - Mean load over interval and instantaneous load

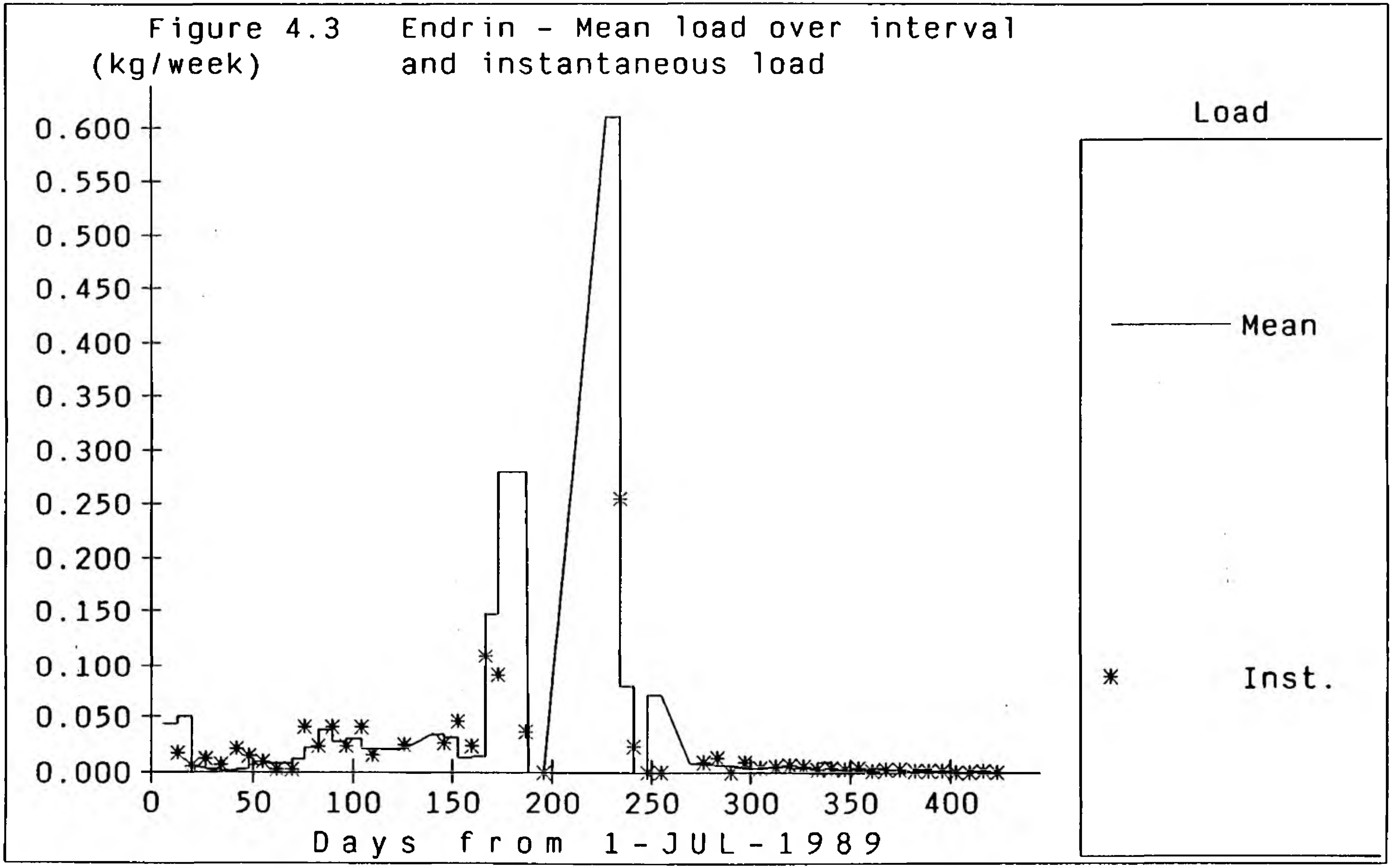


Figure 4.3 Endrin - Mean load over interval and instantaneous load

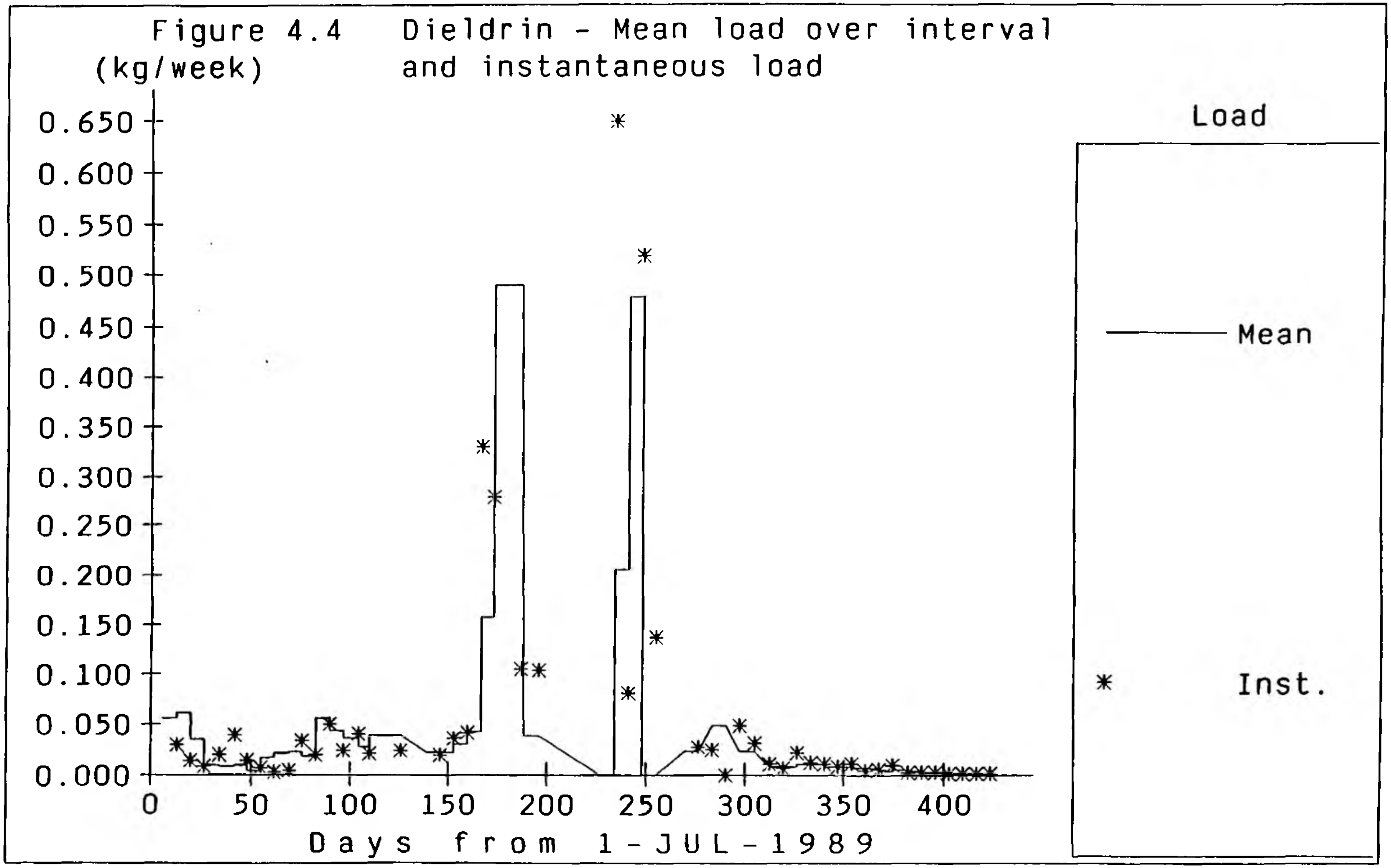


Figure 4.4 Dieldrin - Mean load over interval and instantaneous load

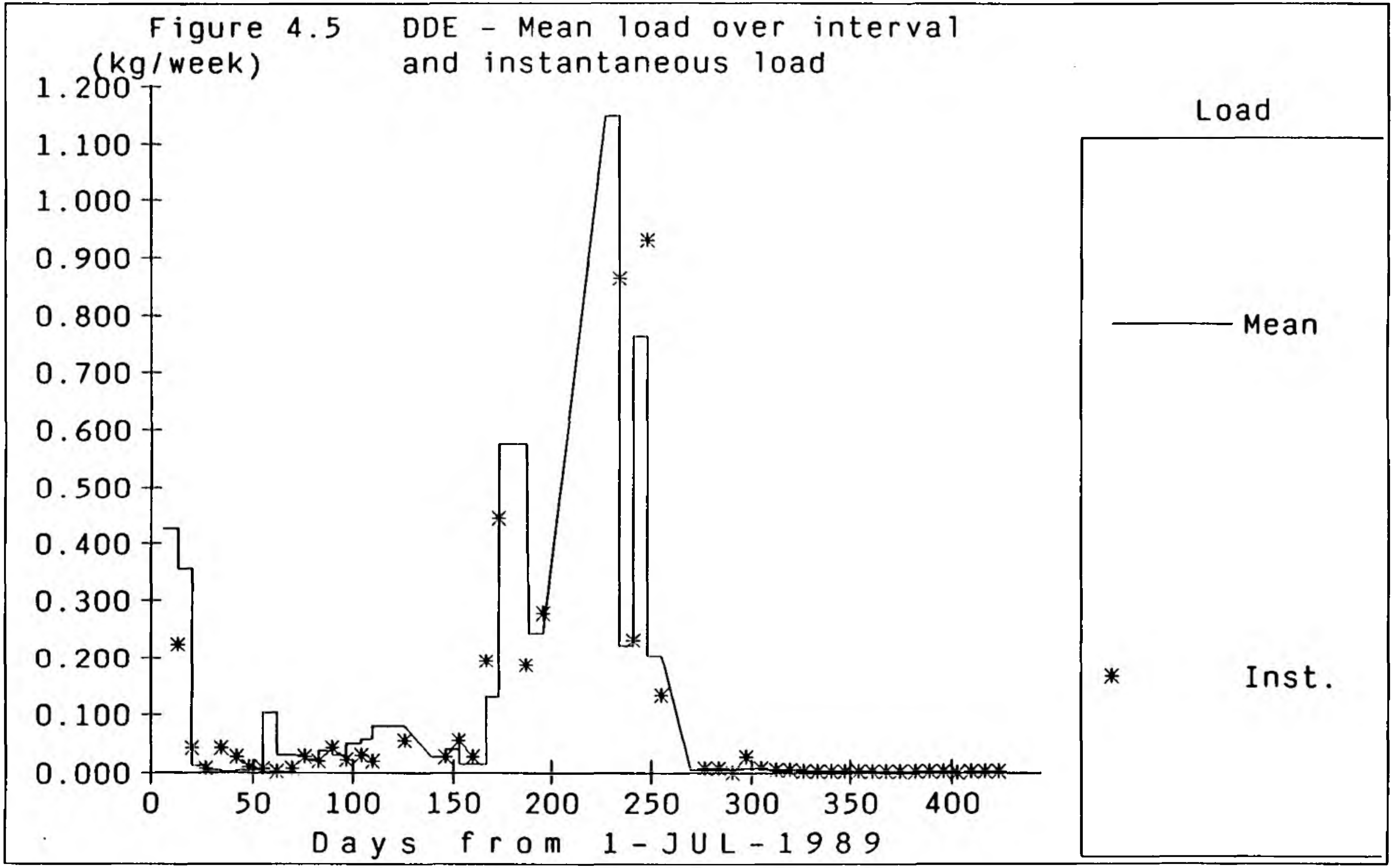


Figure 4.5 DDE - Mean load over interval and instantaneous load

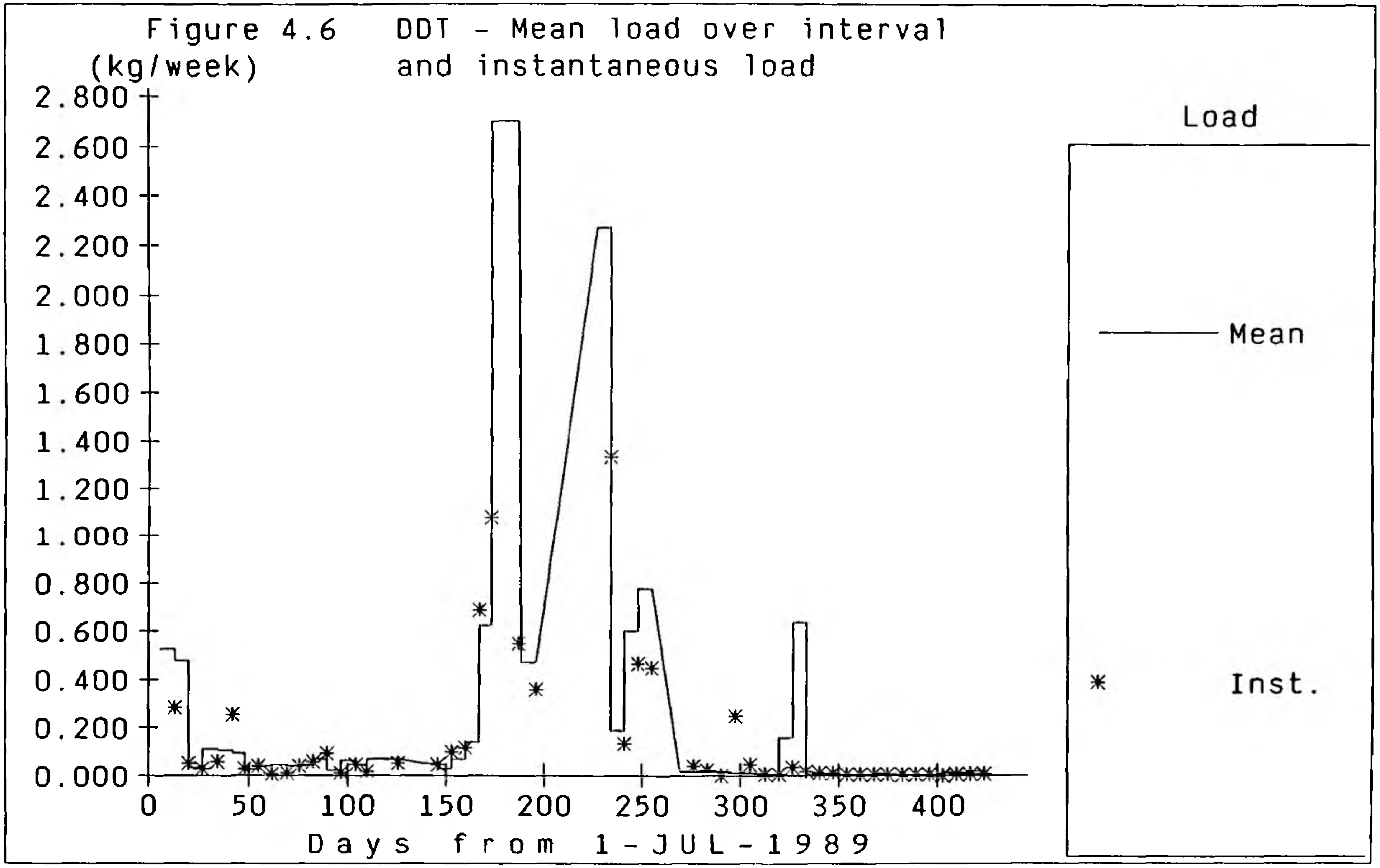


Figure 4.6 DDT - Mean load over interval and instantaneous load

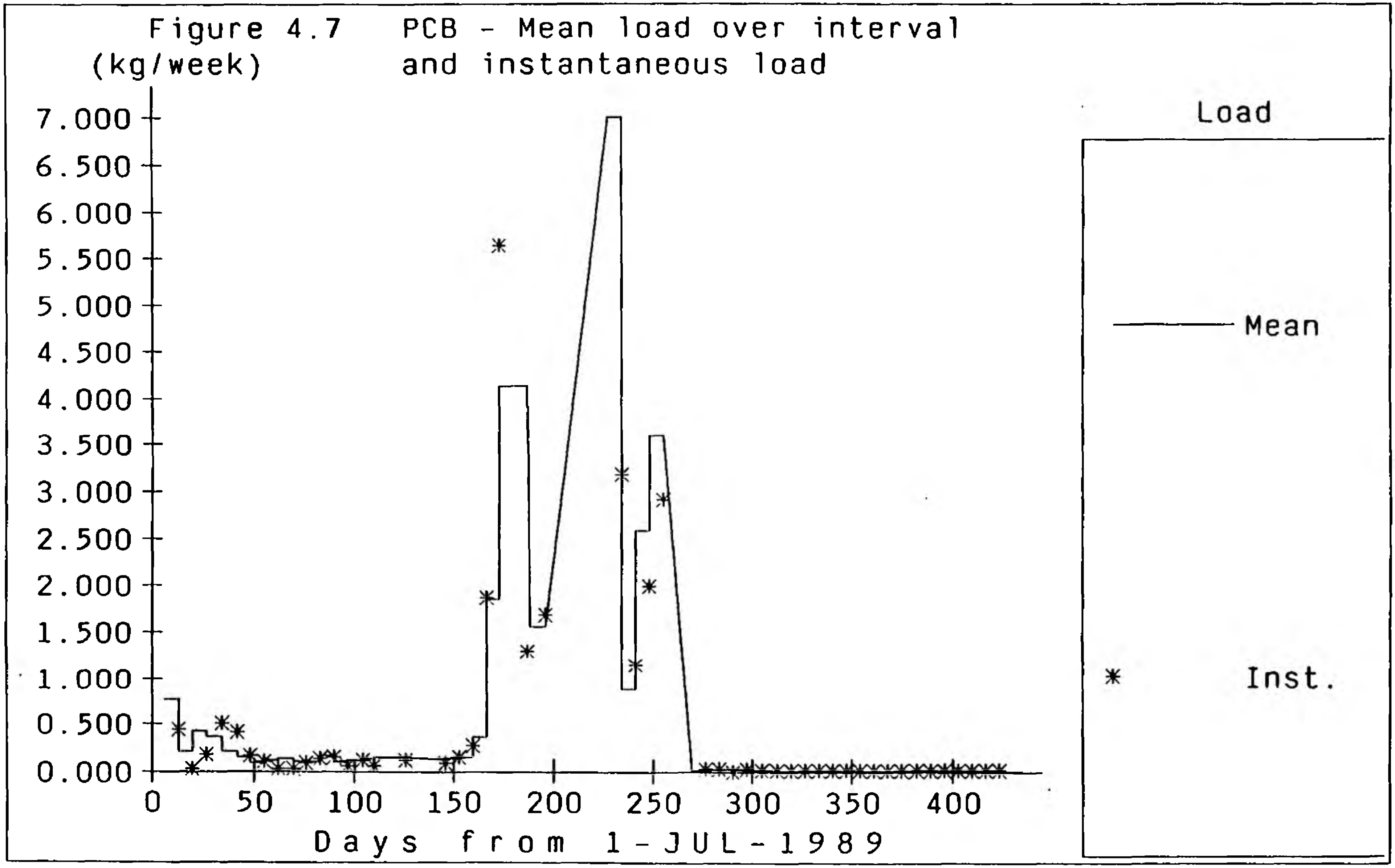


Figure 4.7 PCB - Mean load over interval and instantaneous load

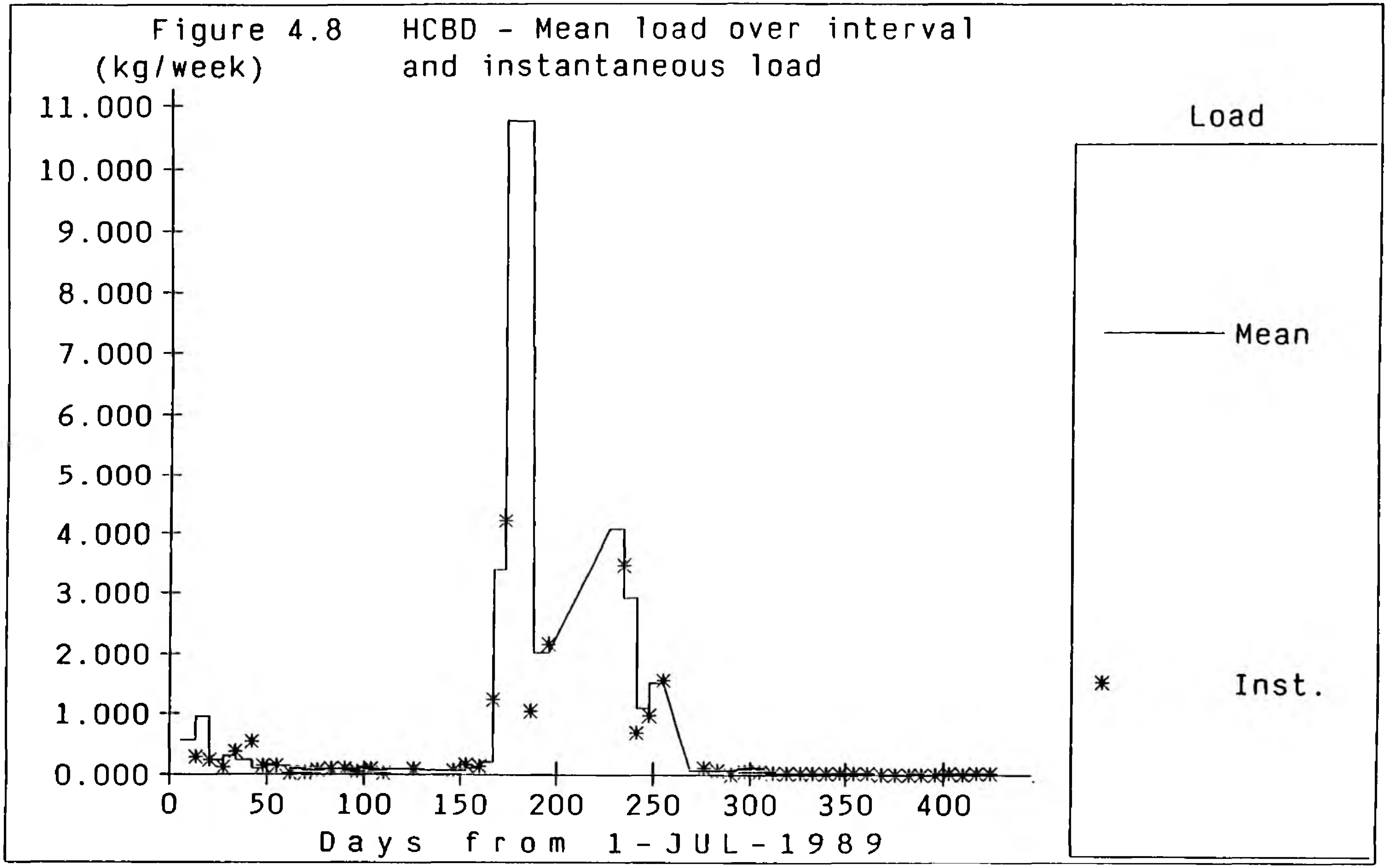


Figure 4.8 HCBD - Mean load over interval and instantaneous load

Figure 4.9 HCB - Mean load over interval and instantaneous load

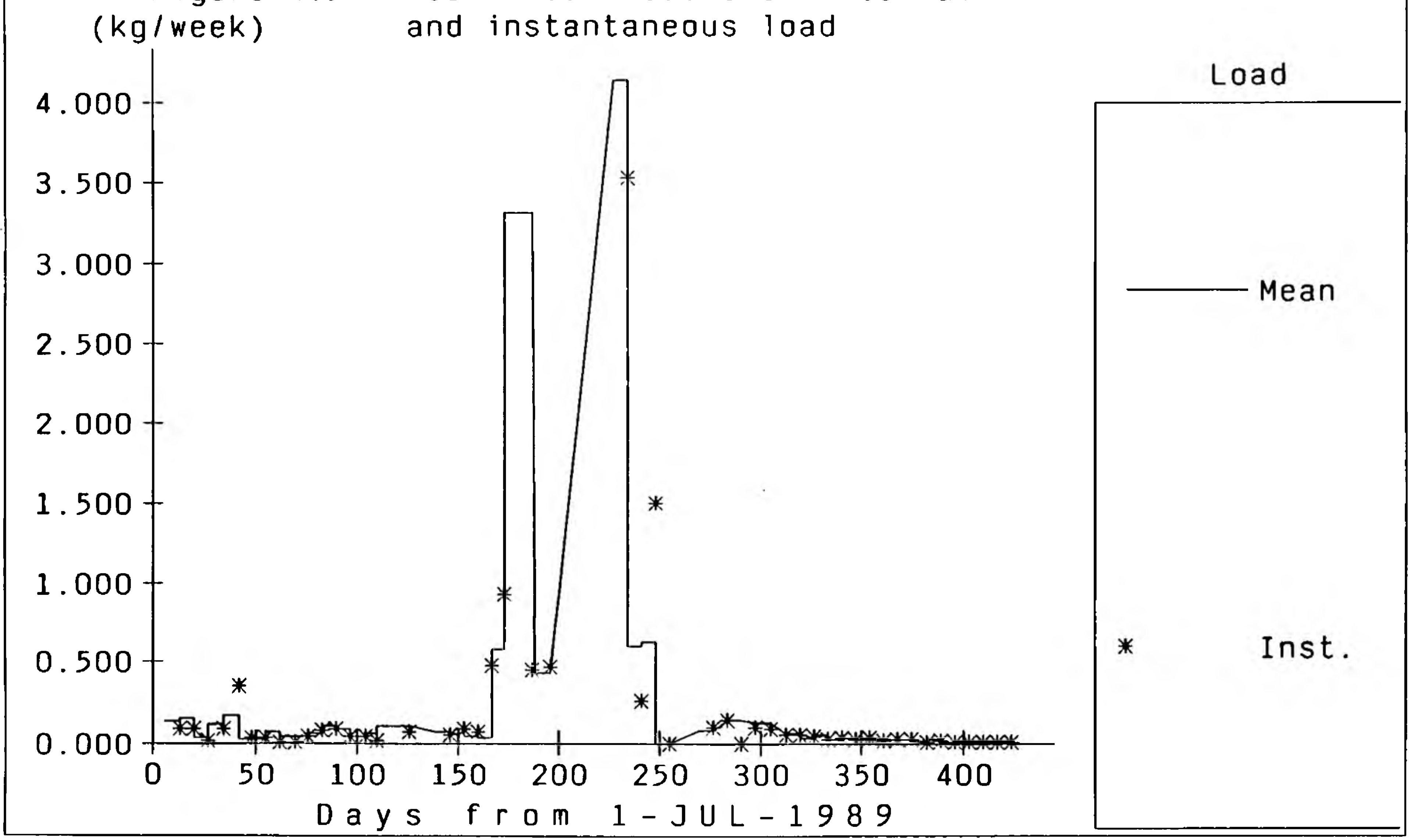
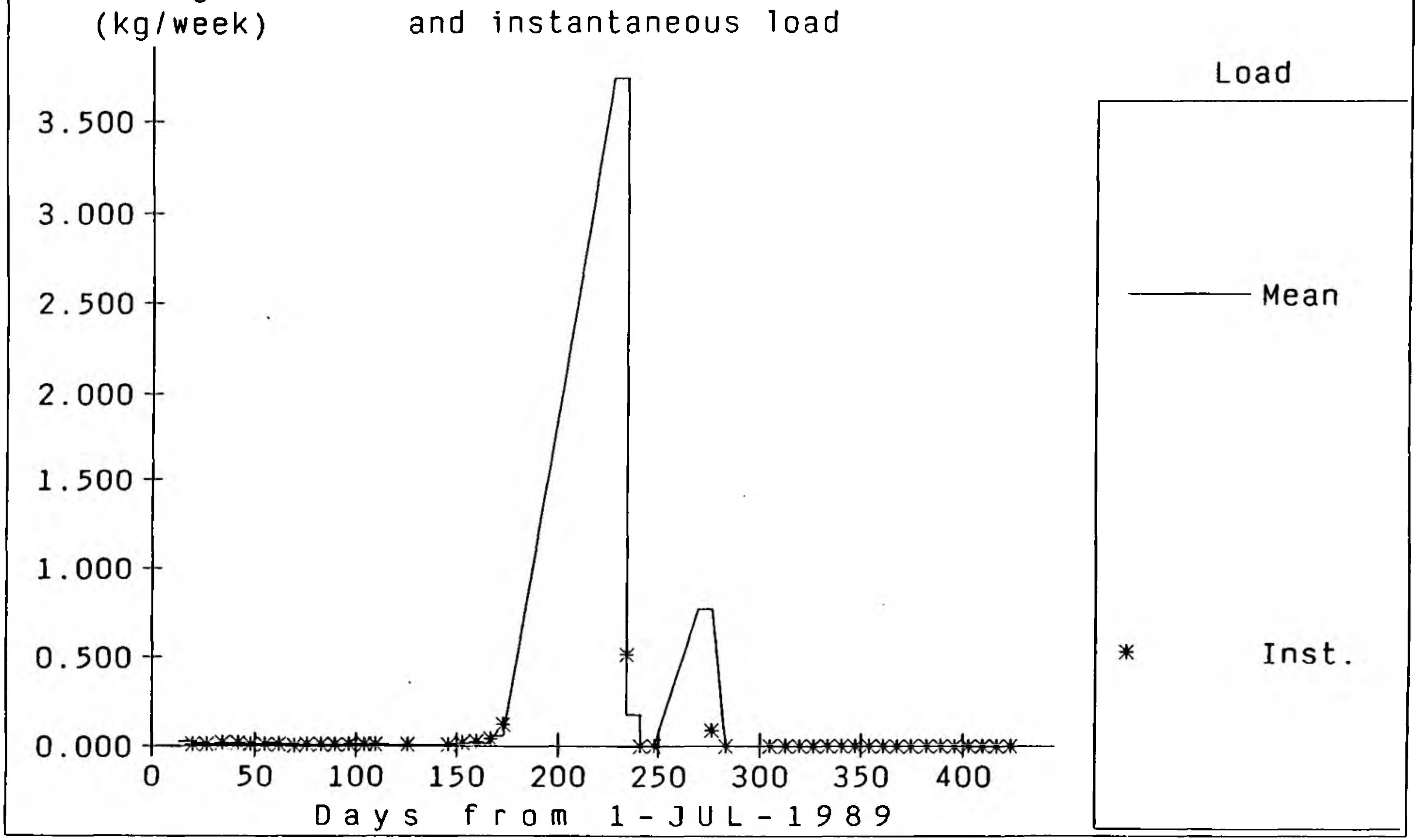


Figure 4.10 Trifluralin - Mean load over interval and instantaneous load



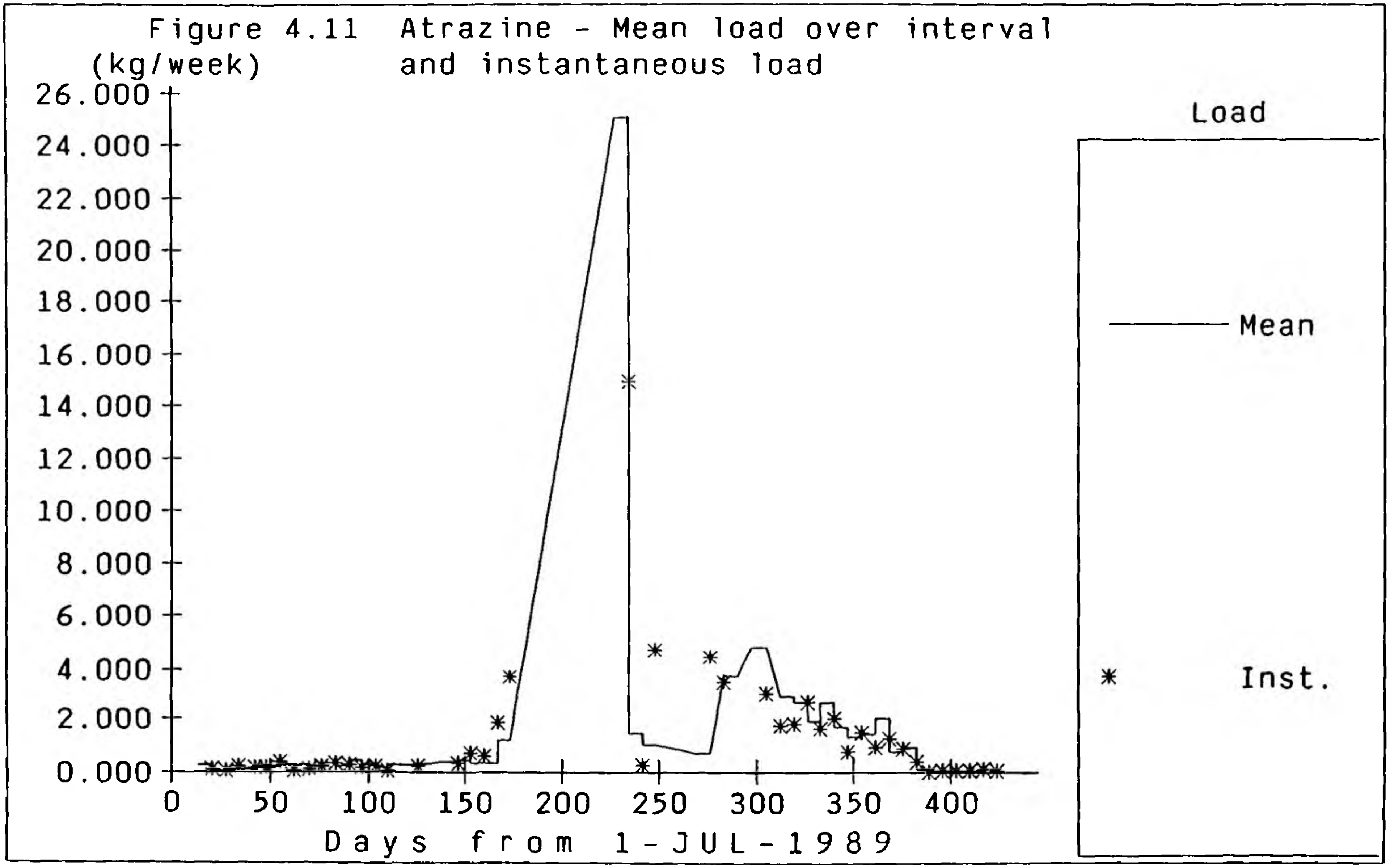


Figure 4.11 Atrazine - Mean load over interval and instantaneous load

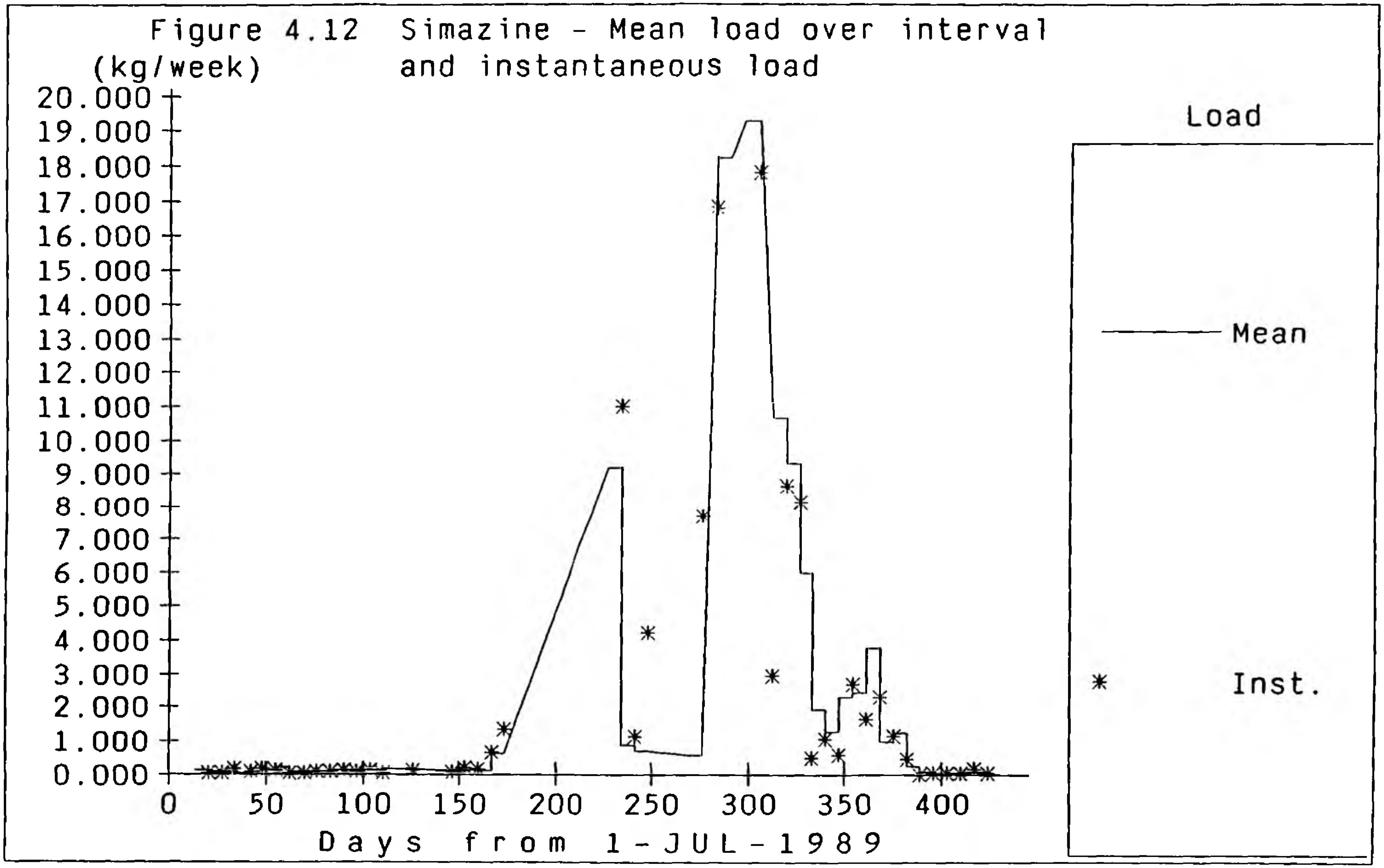


Figure 4.12 Simazine - Mean load over interval and instantaneous load

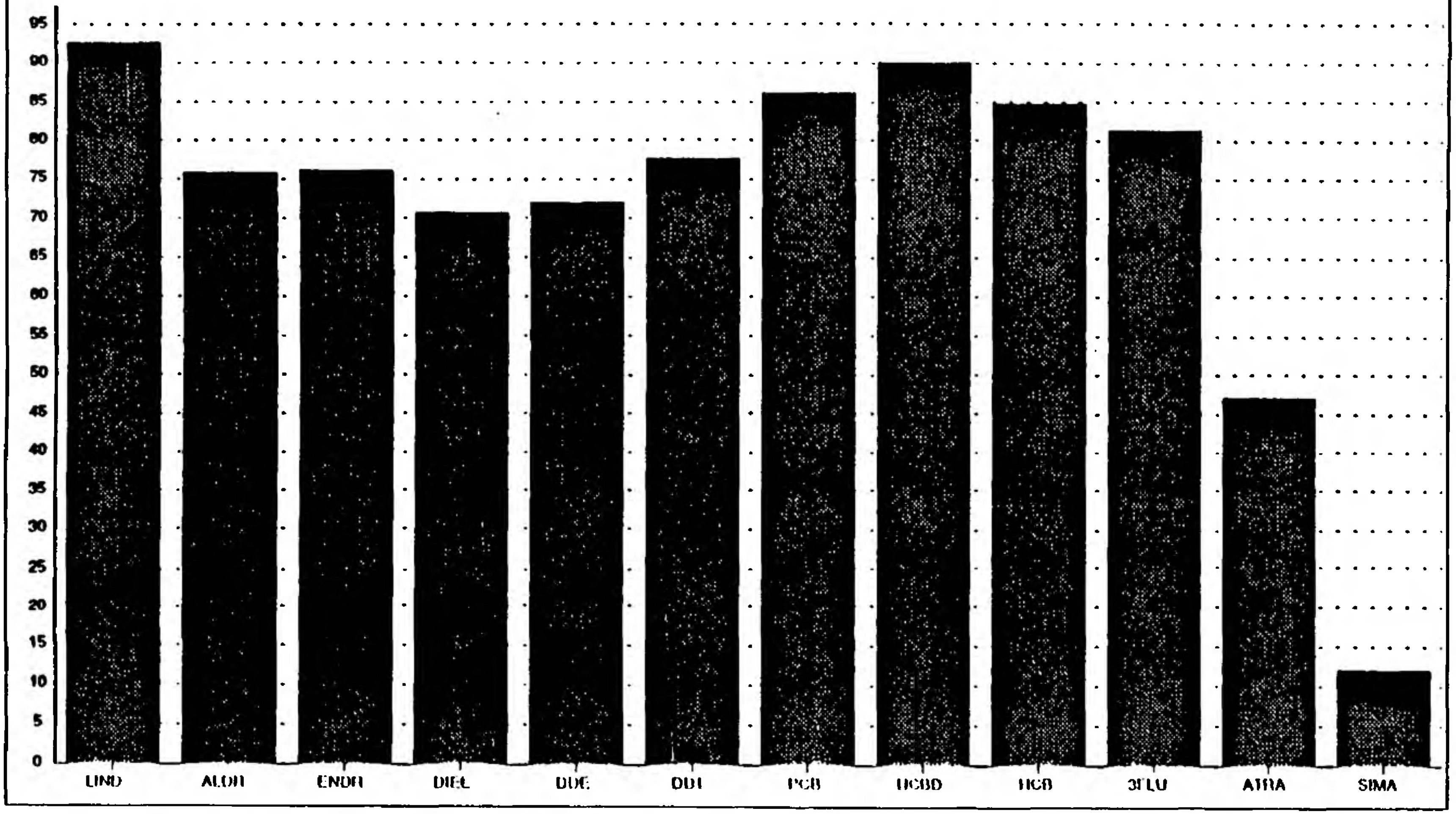
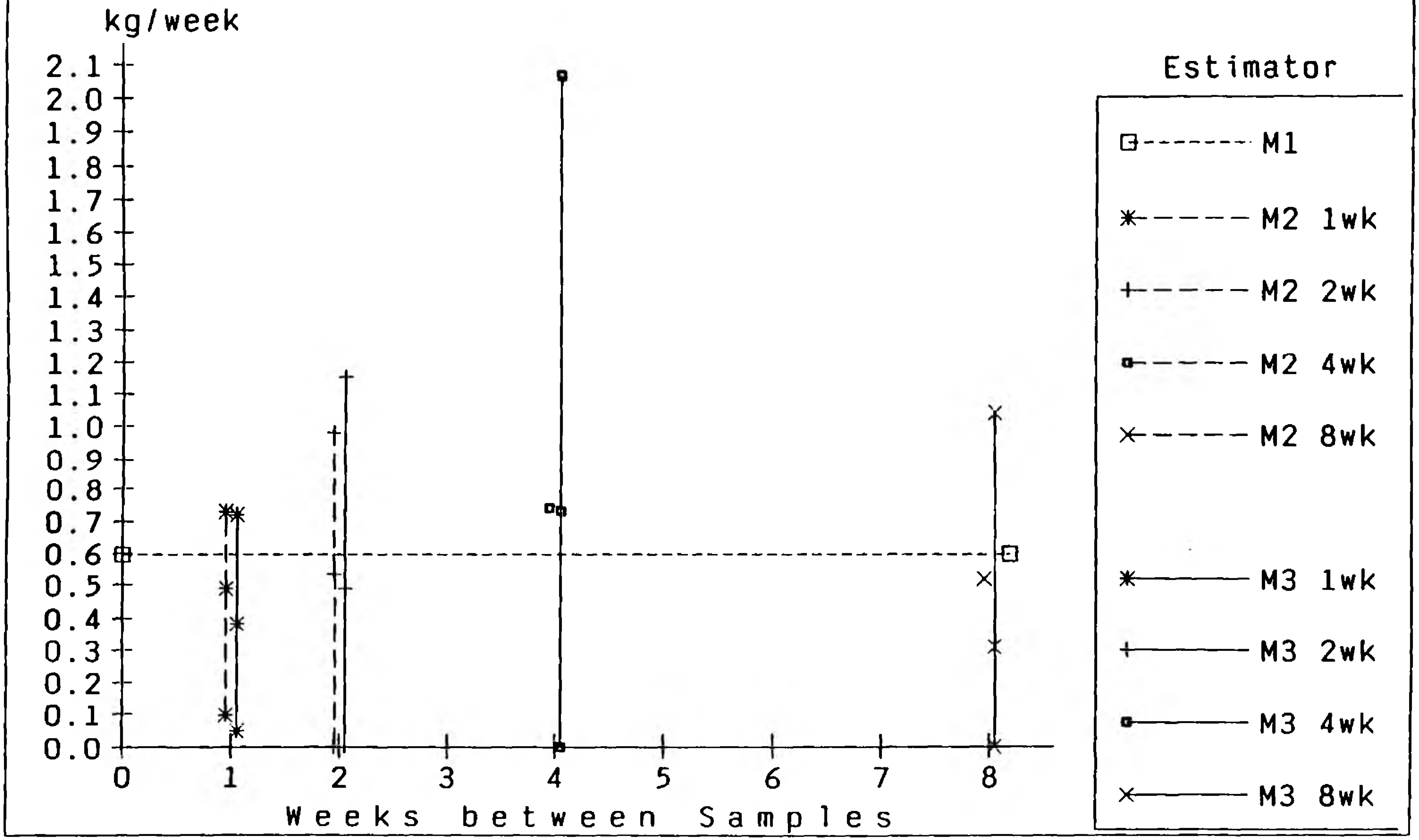


Figure 5 Load in Period B

as percentage of total load

Figure 6.1 Lindane - Load estimates with 95% conf.limits



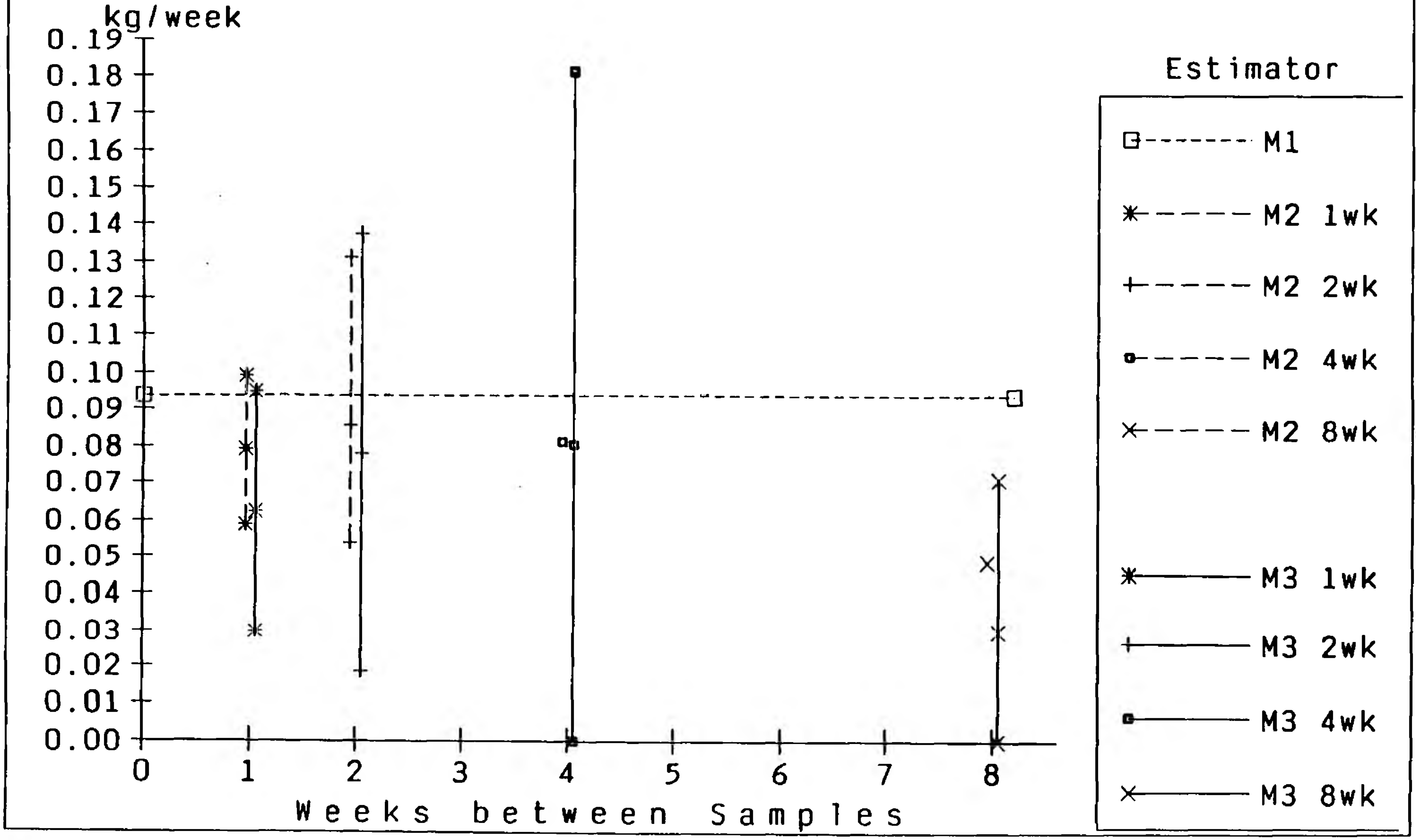
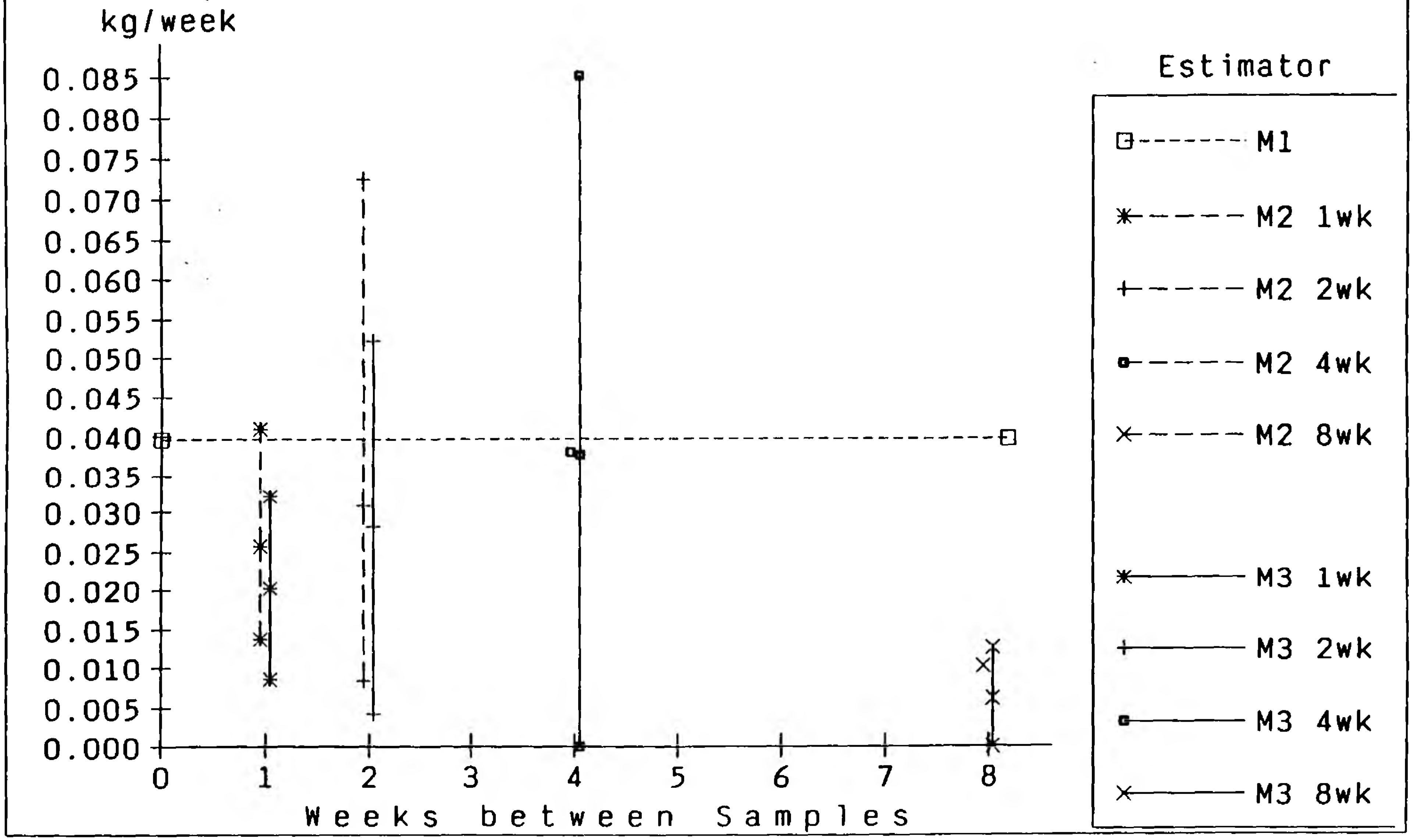


Figure 6.2 Aldrin - Load estimates with 95% conf.limits

Figure 6.3 Endrin - Load estimates with 95% conf.limits



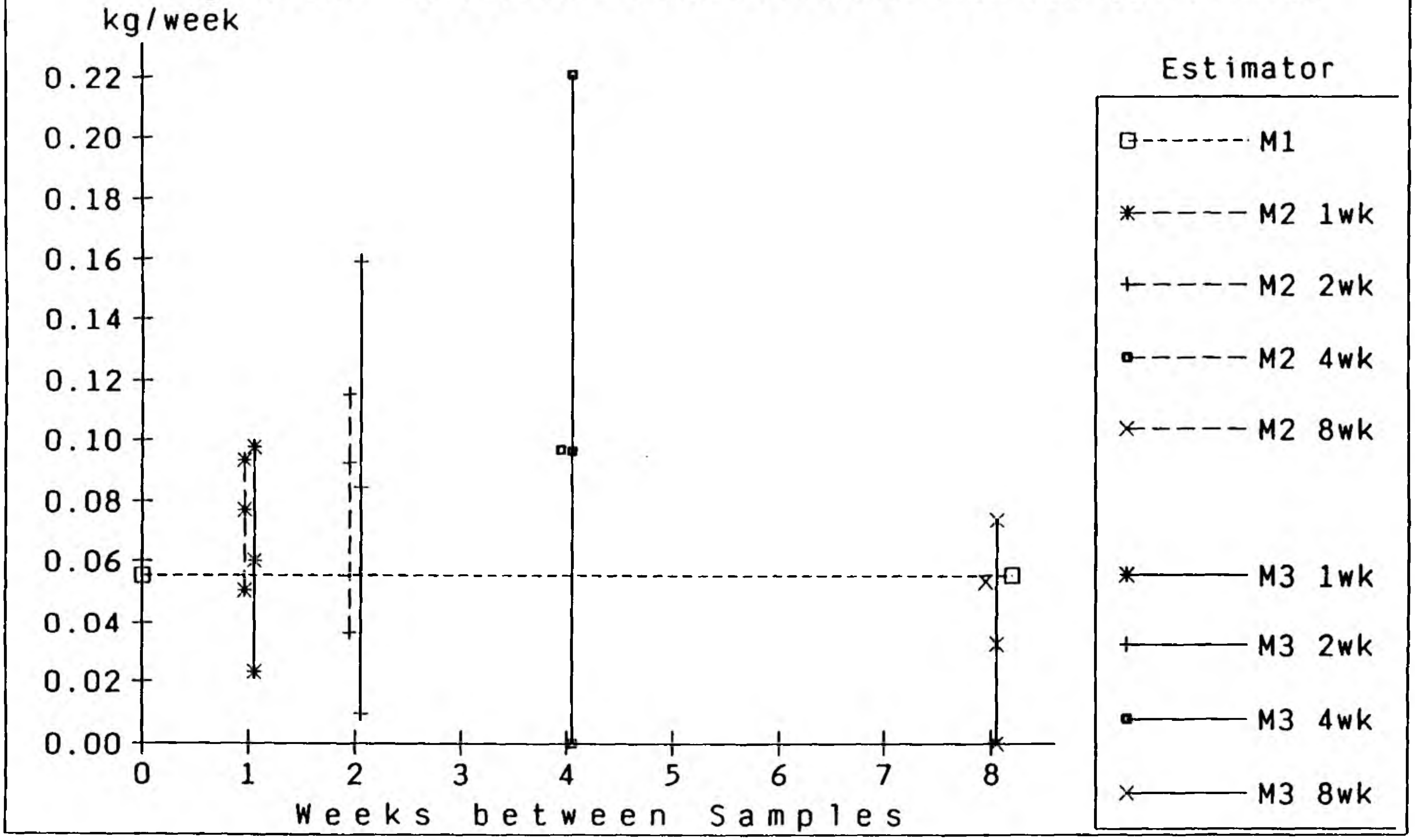


Figure 6.4 Dieldrin - Load estimates with 95% conf.limits

Figure 6.5 DDE - Load estimates with 95% conf.limits

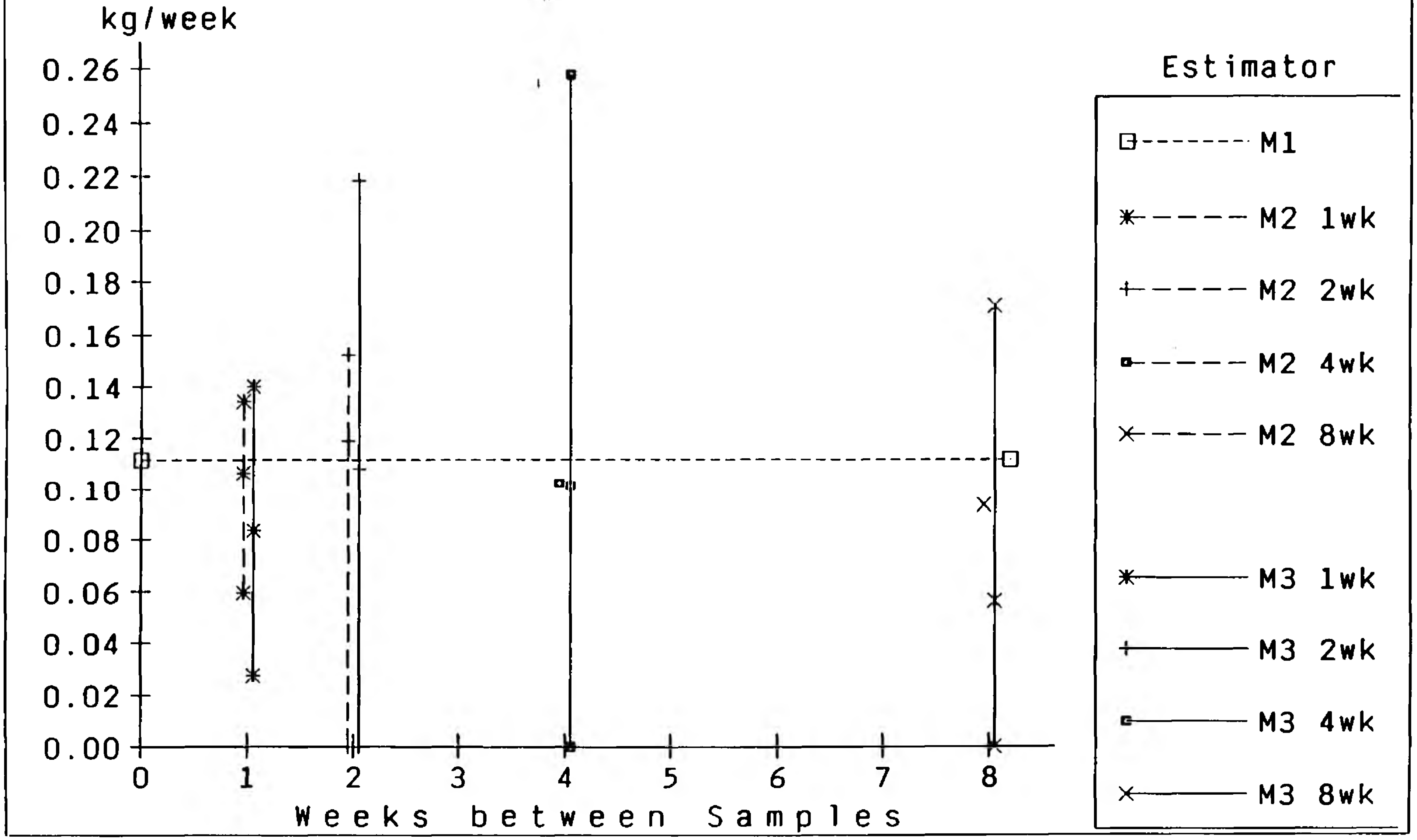


Figure 6.6 DDT - Load estimates with 95% conf.limits

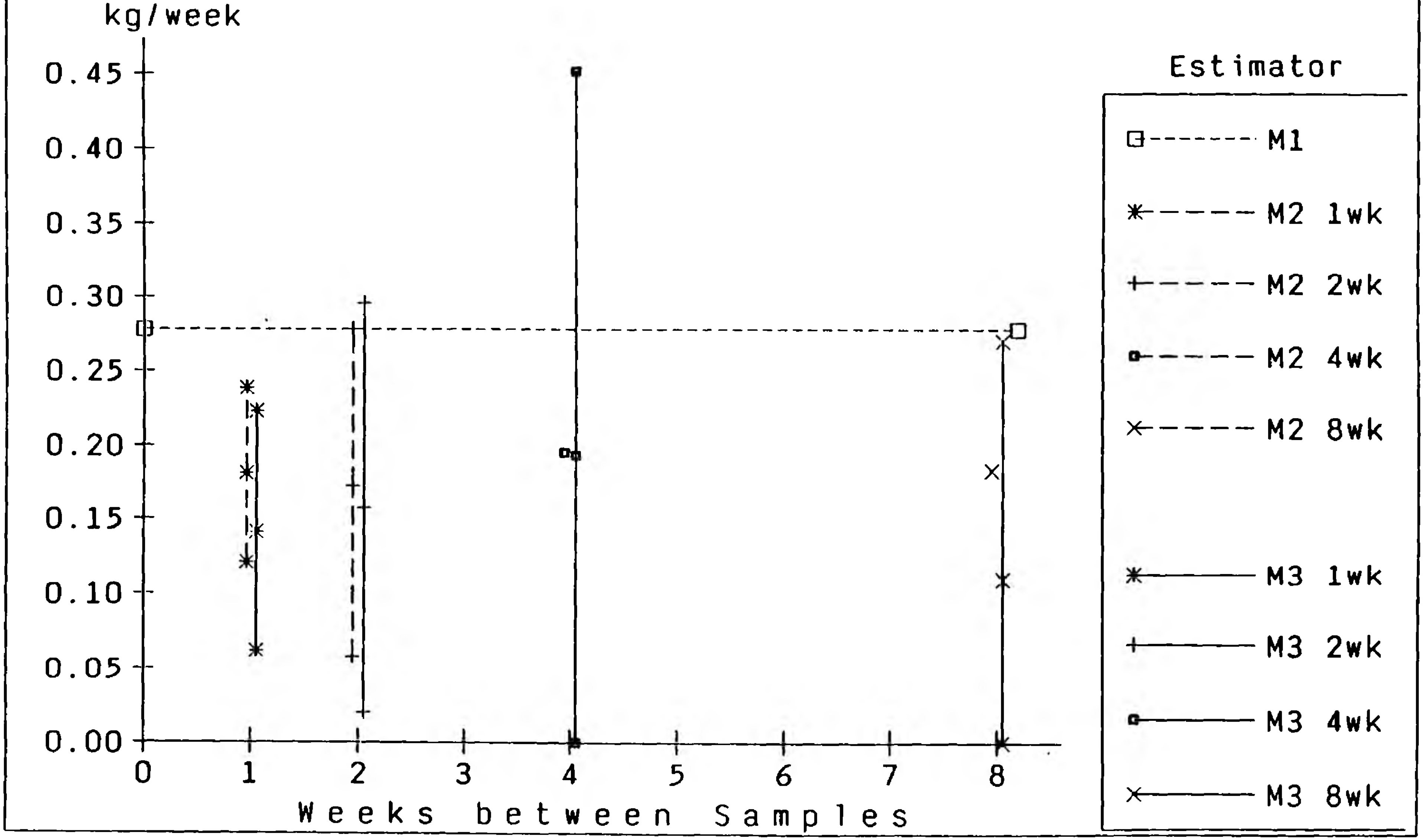
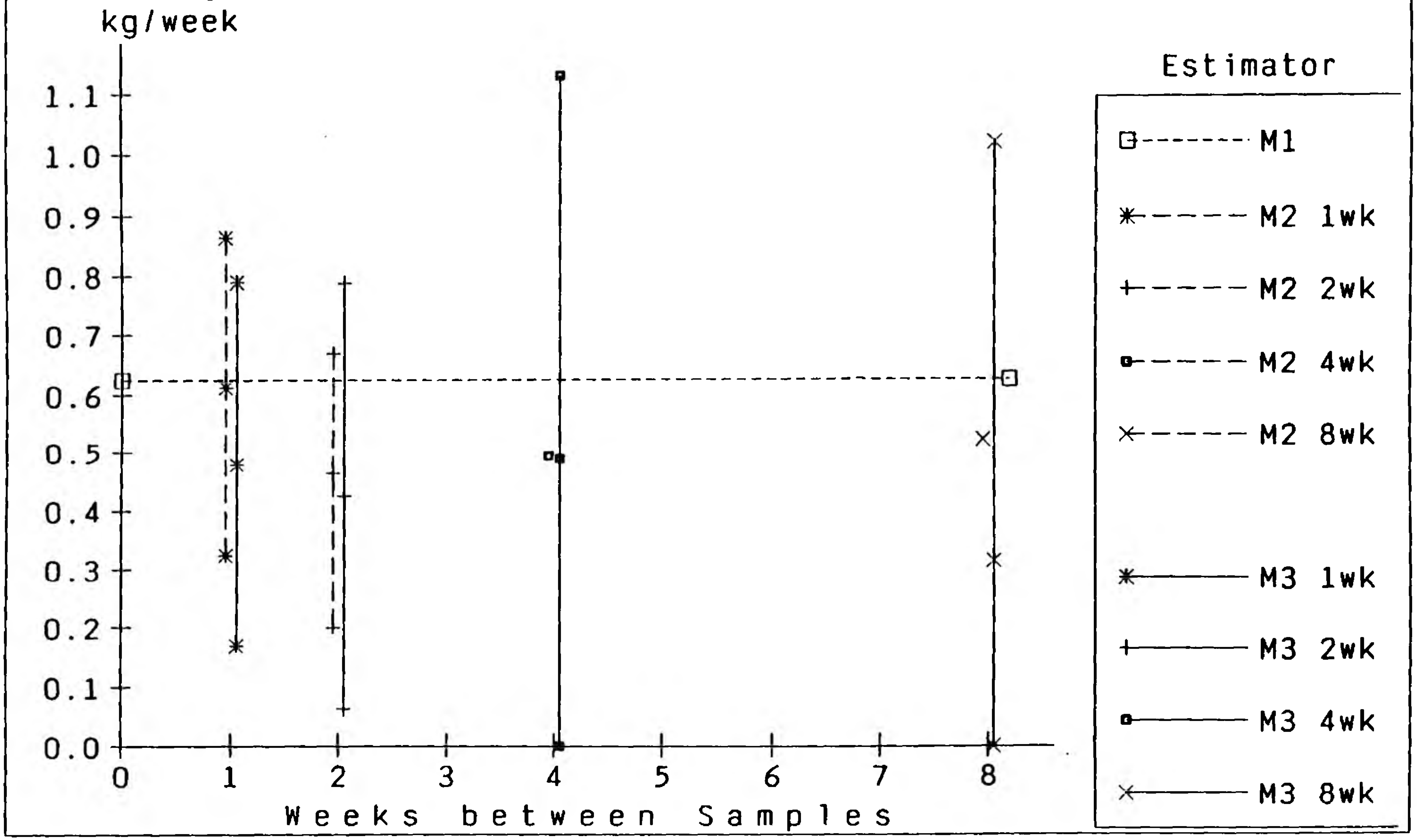


Figure 6.7 PCB - Load estimates with 95% conf.limits



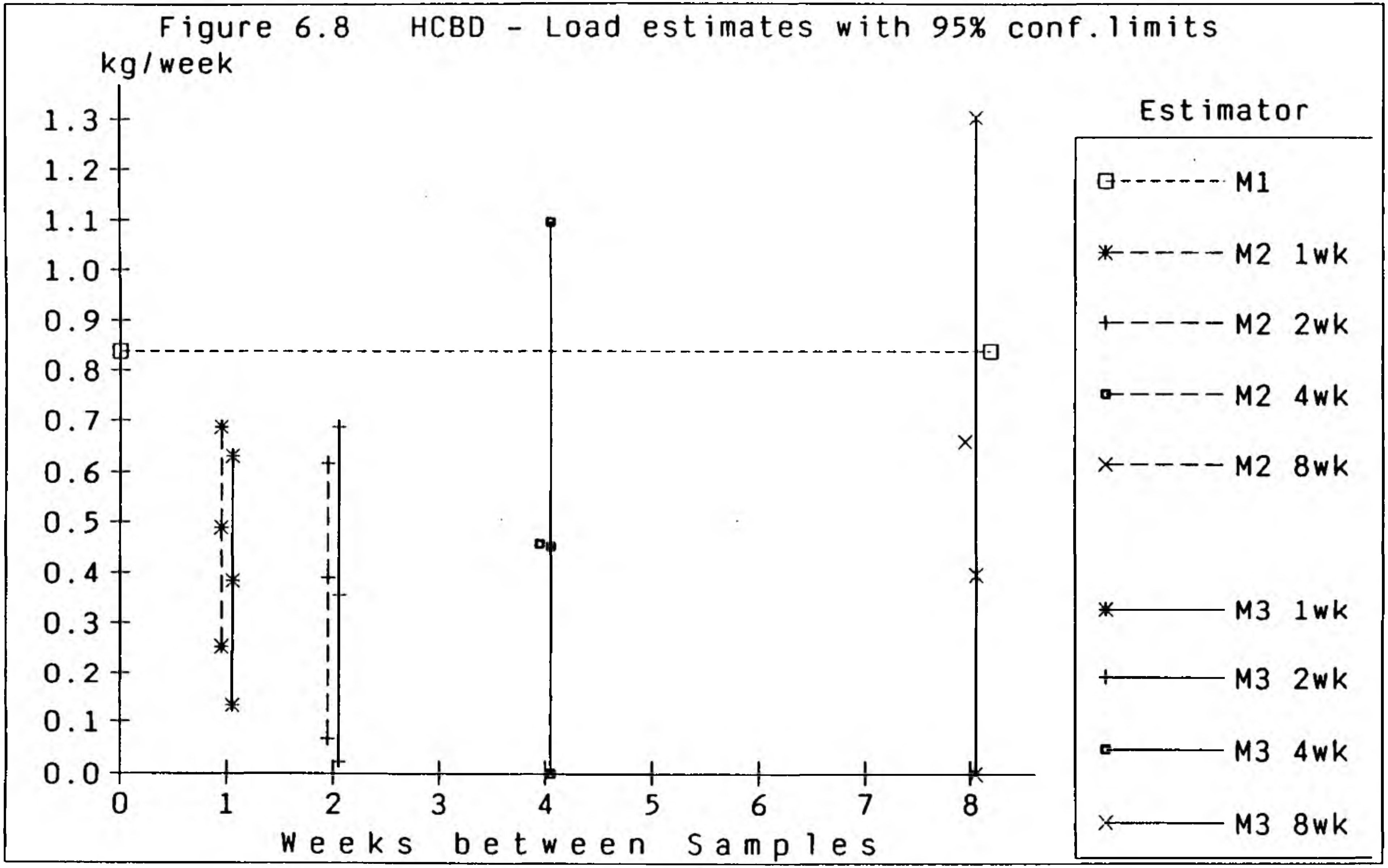


Figure 6.8 HCBD - Load estimates with 95% conf.limits

Figure 6.9 HCB - Load estimates with 95% conf.limits

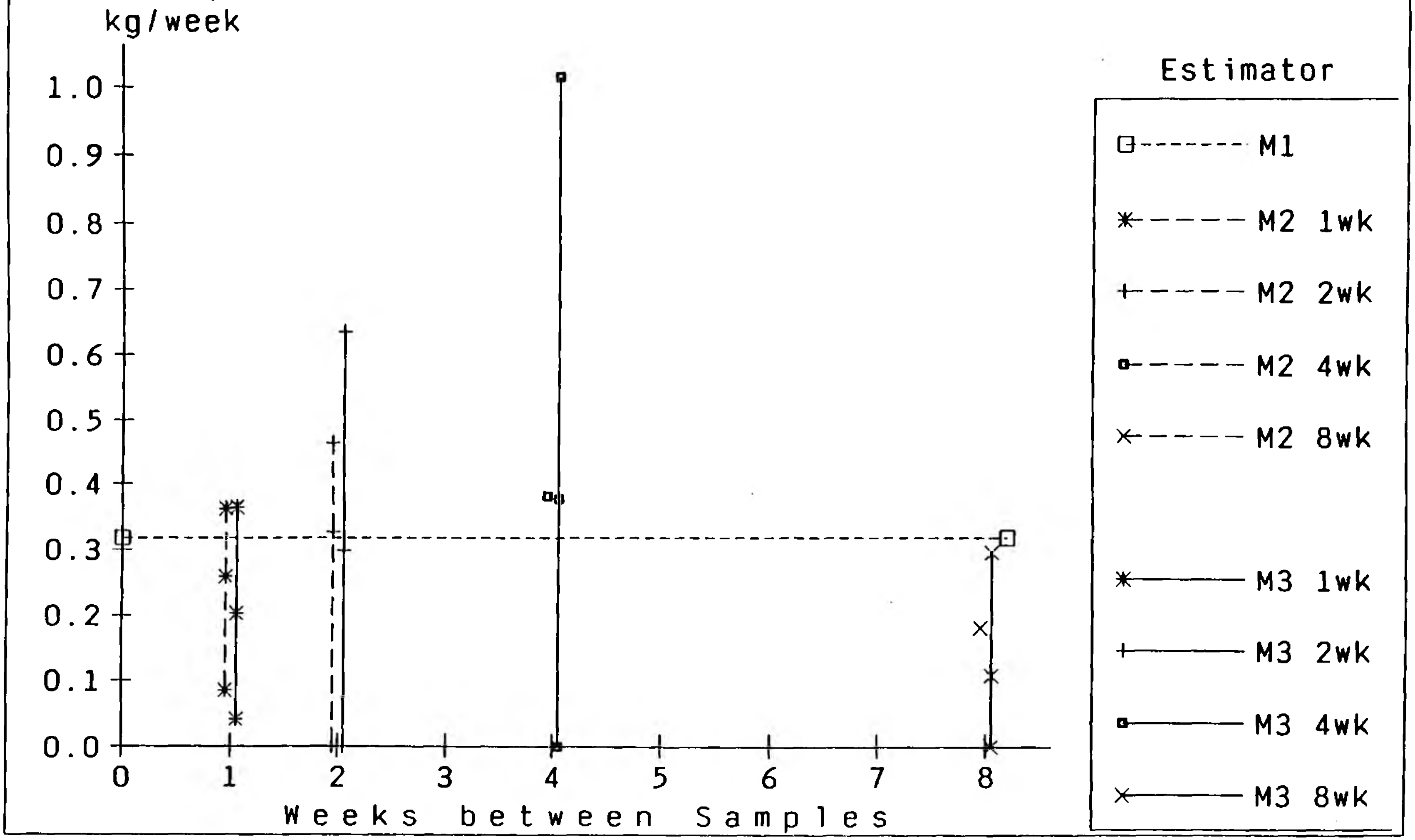
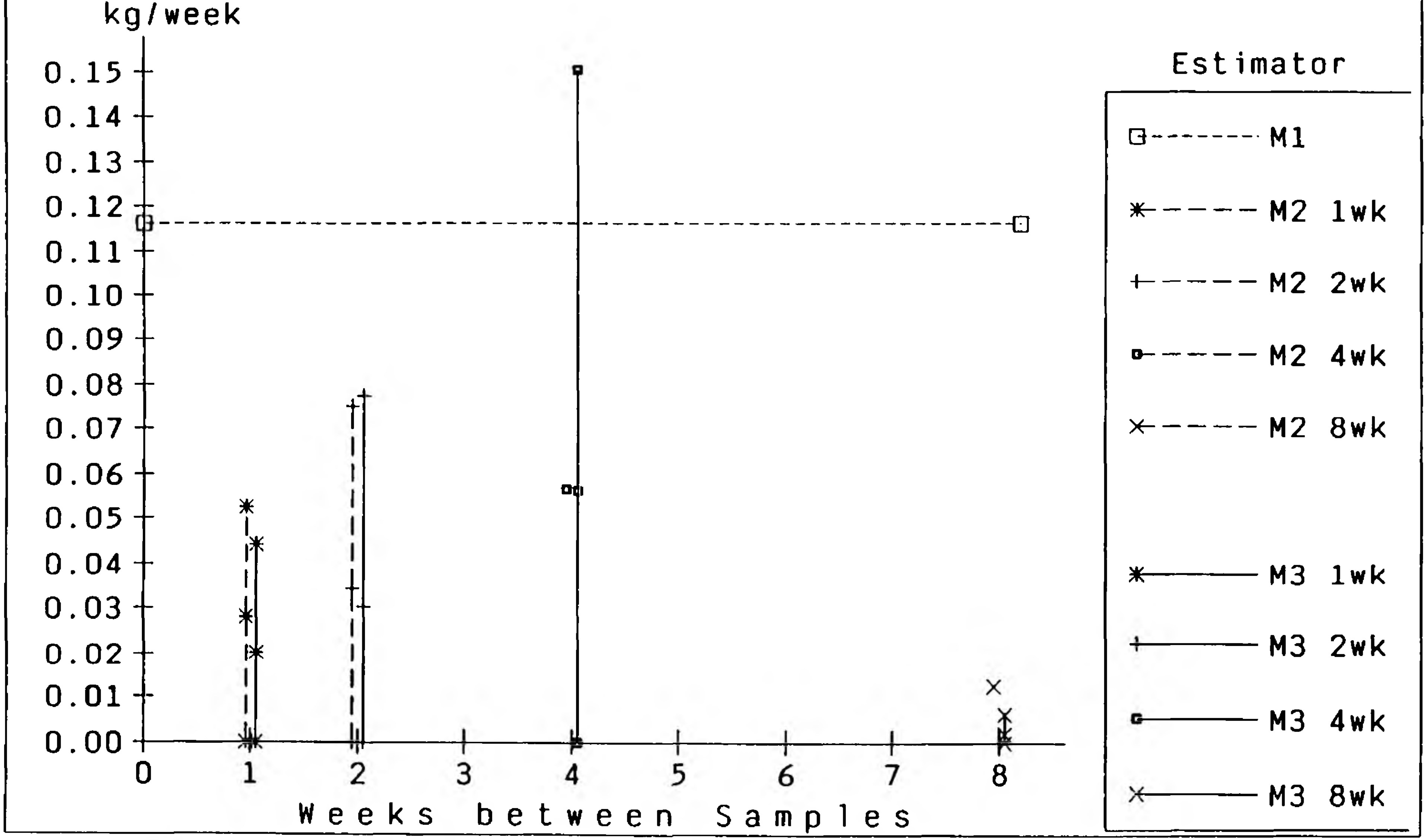


Figure 6.10 Trifluralin - Load estimates with 95% conf.lim



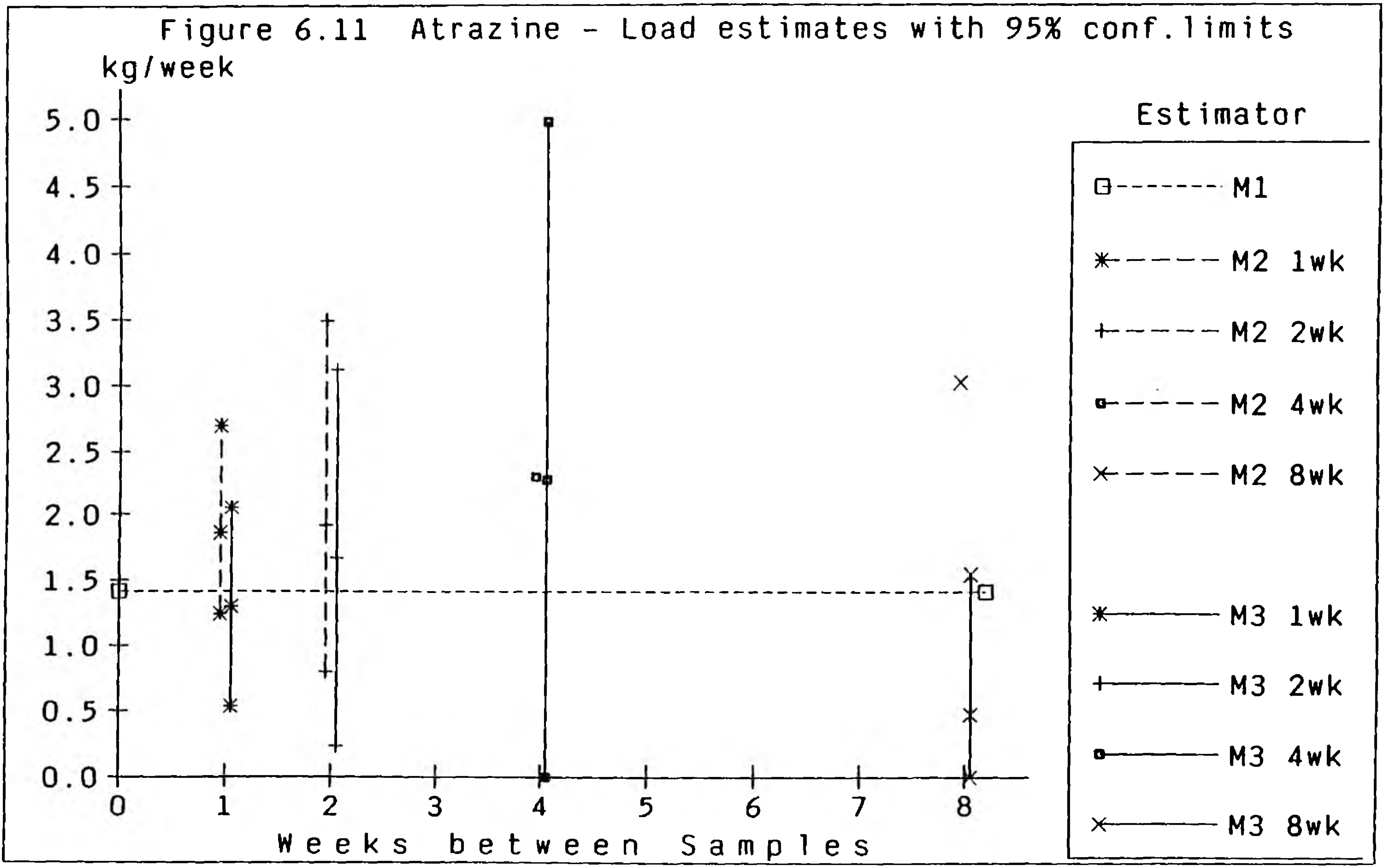


Figure 6.11 Atrazine - Load estimates with 95% conf.limits

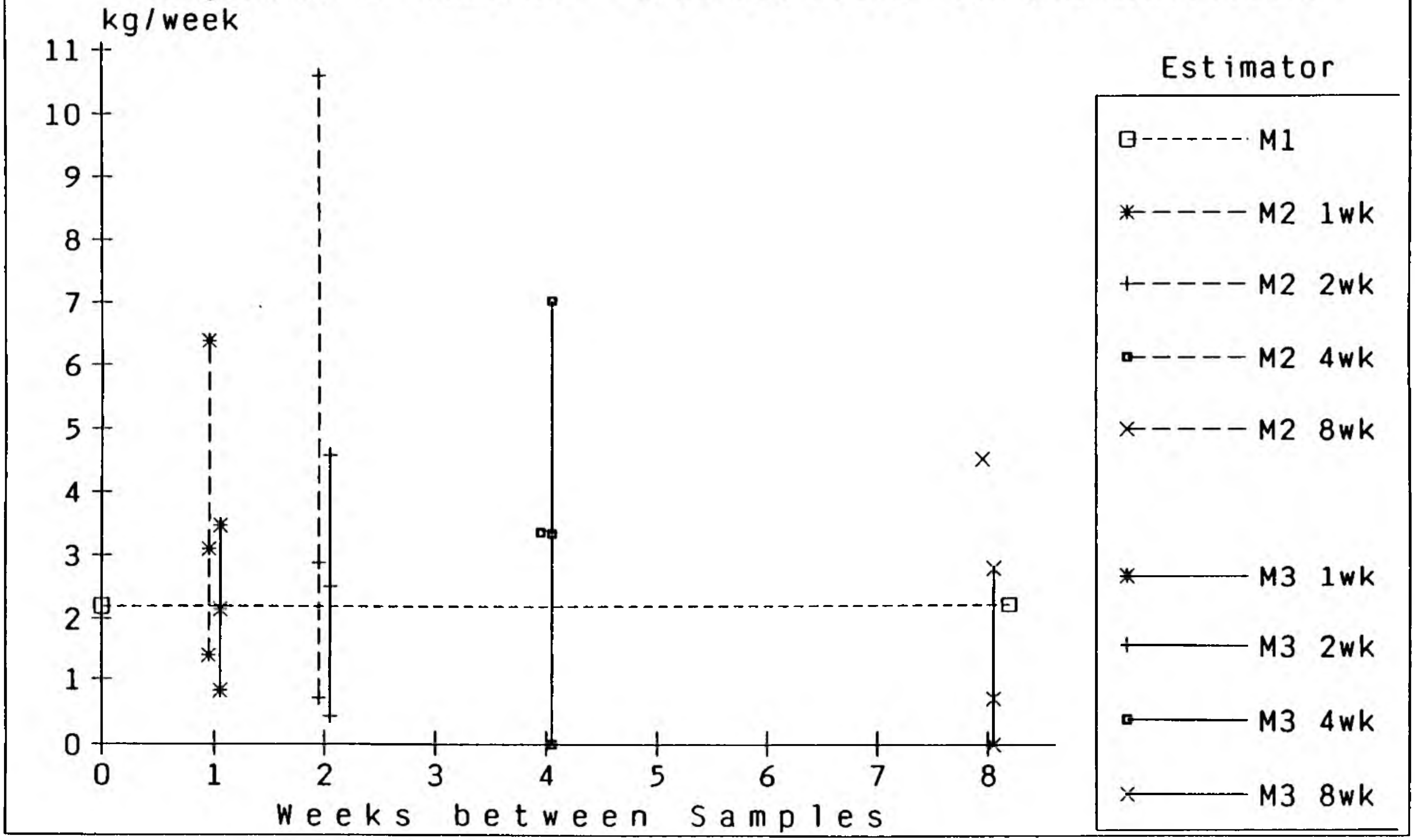


Figure 6.12 Simazine - Load estimates with 95% conf.limits