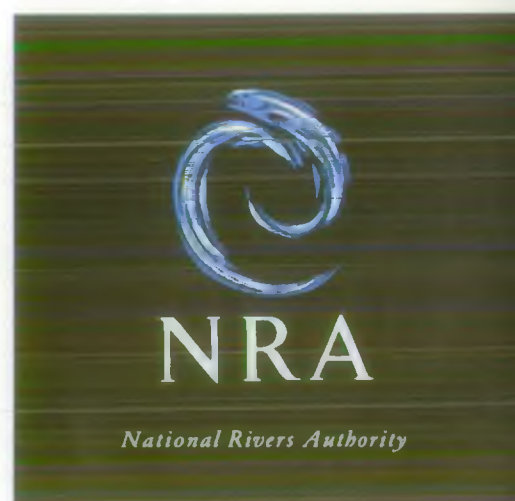


Comparison of Load Estimation from Grab and Flow-proportioning Samples

WRc plc

R&D P-19



COMPARISON OF LOAD ESTIMATION FROM GRAB SAMPLES AND FLOW-PROPORTIONAL SAMPLING

National Rivers Authority
Information Centre
Head Office

Class No

Accession No AMBU

Report No: PRS 2383-M

February 1990

Authors: R M Harrison and G A Thorogood - University of Essex

R F Lacey

Contract Manager: T F Zabel

Contract No: 4755/2826/9378

Clients Reference No: 8.1.2a/7.1.0c/PECD 7/7/220

This study was undertaken partly under contract to the Department of the Environment and partly under contract to the National Rivers Authority and equivalent bodies in Scotland and Northern Ireland, and was released to the Public Domain on 20 December 1990.

Any enquiries relating to this report should be referred to the author at the following address:

WRc plc, Henley Road, Medmenham, PO Box 16, Marlow, Buckinghamshire
SL7 2HD. Telephone: Henley (0491) 571531

COMPARISON OF LOAD ESTIMATION FROM GRAB SAMPLES AND FLOW-PROPORTIONAL SAMPLING

R M Harrison, G A Thorogood and R F Lacey

SUMMARY

The principal objective of this study was to compare estimates of load based on discrete data (grab samples and instantaneous measurements of flow) with those based on continuous monitoring. Subsidiary objectives were to demonstrate the effects of sampling frequency and of choice of method of calculation on the accuracy of estimates, and to check the validity of sampling from a single position in the cross-section of the river.

A continuous flow-proportional sampler was installed at the existing river-gauging station at Kingston upon Thames. The study was based on results obtained from this sampler and from grab samples taken at the same location between June 1987 and December 1988. The samples were analysed for ten determinands. Additional exercises were undertaken to investigate variations in concentration across the section of the river.

The method of load estimation based on continuous flow measurement and flow-proportional sampling eliminates the uncertainty associated with the inability of grab sampling to account fully for temporal variations in concentration and flow. Compared with continuous monitoring, estimates of annual load based on weekly grab sampling were shown to be accurate only to within $\pm 25\%$, while estimates based on monthly sampling could easily err by as much as $\pm 50\%$.

The Thames at Kingston appeared to be well enough mixed in cross section for a single sampling point to be representative of the total flow. The possible error in load estimation arising from incomplete mixing was judged to be smaller than $\pm 10\%$.

Report No PRS 2383-M, February 1990

31 Pages, 28 Figures, 9 Tables, 4 Appendices

Project reference: 8.1.2a

CONTENTS

	Page
SUMMARY	(1)
SECTION 1 - INTRODUCTION	1
1.1 BACKGROUND	1
1.2 OBJECTIVES	2
SECTION 2 - METHODS	3
2.1 SAMPLING EQUIPMENT	3
2.2 PRELIMINARY TESTS	3
2.3 FLOW PROPORTIONAL SAMPLING	4
2.4 CROSS RIVER SAMPLING	5
2.5 ANALYTICAL PROCEDURES	6
2.6 TESTS FOR PRECISION OF ANALYSIS	8
2.6.1 Trace metals	8
2.6.2 Total phosphorus (TP), soluble reactive phosphate (SRP) and nitrate	8
SECTION 3 - RESULTS OF CROSS RIVER SAMPLING	10
3.1 SAMPLING VARIATION AT A SINGLE POINT	10
3.2 VARIATION ACROSS SECTION OF RIVER	10
SECTION 4 - ESTIMATION OF LOAD	16
4.1 AVAILABLE DATA	16
4.2 COMPARISON OF METHODS	17
4.3 DETAILS OF METHODS	17
4.4 STATISTICAL ASSUMPTIONS AND RESERVATIONS	22
4.5 RESULTS OF COMPARISON	22

CONTENTS - continued

	Page
SECTION 5 - RELATIONSHIPS BETWEEN CONCENTRATIONS, FLOW AND SUSPENDED SOLIDS	26
5.1 CONCENTRATIONS AND FLOW	26
5.2 CONCENTRATIONS AND SUSPENDED SOLIDS	27
SECTION 6 - DISCUSSION	27
SECTION 7 - CONCLUSIONS	30
ACKNOWLEDGEMENT	30
REFERENCES	31

FIGURES

APPENDICES

- A. TRACE ELEMENT AND SUSPENDED SOLIDS CONCENTRATIONS IN COMPOSITE AND GRAB SAMPLES, AND FLOWS DURING JUNE 1987 TO DECEMBER 1988**
- B. TOTAL PHOSPHORUS, SOLUBLE REACTIVE PHOSPHATE AND NITRATE CONCENTRATIONS IN COMPOSITE AND GRAB SAMPLES, AND FLOWS DURING FEBRUARY 1988 TO DECEMBER 1988**
- C. POSSIBLE BIAS IN METHOD 2**
- D. COMPARISON OF CONFIDENCE INTERVALS CALCULATED BY DIFFERENT METHODS**

SECTION 1 - INTRODUCTION

1.1 BACKGROUND

There is increasing concern about the discharge of pollutants to the marine environment. Rivers are an important route by which such substances may be conveyed to the sea. The control of marine pollution can therefore be logically discussed only if information is available on the sizes of river-borne loads and on the accuracy with which these loads have been estimated.

The load of a given substance transported by a particular river is usually calculated by combining information about the water discharge rate (usually measured continuously) with information about the concentrations of the specific substance obtained from a limited number of grab samples. Difficulties and uncertainties are associated with this process because of the temporal variations in concentration and flow. These raise questions not only of what frequency of sampling is needed (Ellis and Lacey 1980) but also of exactly how the sample data should be combined to arrive at the estimate of load (Walling and Webb 1985). Additional but separate difficulties may arise if the sampling takes place at a location where the river can not be assumed to be completely mixed across the whole of its section.

Factors that give rise to errors of estimation can be of two different kinds, according to whether their effects are systematic or random. In general it is desirable to avoid systematic errors as far as possible since, in the context of load estimation, they could lead to wrong decisions about the most appropriate methods of pollution control. Random errors, provided that they have been statistically quantified, are less problematic and their effects can often be mitigated by making additional measurements. Methods for coping with the uncertainty associated with them are well established.

Some of the problems of estimation of contaminant loads have been previously discussed by Walling and Webb (1985), but the numerical

results in their paper were concerned only with suspended solids. No studies have been reported comparing methods of load estimation for other determinands, such as heavy metals. In particular, no studies have directly compared results based on grab sampling on a limited number of occasions with those from the 'ideal' system of continuous flow-proportional sampling.

In view of the need for better understanding of the problems of load estimation, the Department of the Environment (DoE) and the Water Research Centre (WRC) agreed to undertake the research described in this report. The programme of sampling and analysis was carried out by the University of Essex under contract to WRC and DoE.

1.2 OBJECTIVES

The objectives of this study were:

- 1) to establish a flow-proportional sampler at Kingston upon Thames and procedures to enable the estimation of loads based on continuous measurements of flow and concentration;
- 2) to investigate whether concentrations measured at the continuous sampling point were representative of the average concentration across the whole section of the river;
- 3) to compare estimates of load based on grab samples and instantaneous measurements of flow with those based on continuous monitoring;
- 4) to demonstrate the effects of sampling frequency and of choice of method of calculation on the accuracy of the estimates of load based on grab sampling;
- 5) to examine the relationships between the concentrations of chemical determinands, the concentration of suspended solids and the flow of the river, to assess whether these could be used for improving the estimation of loads derived from grab samples.

SECTION 2 - METHODS

2.1 SAMPLING EQUIPMENT

A high volume plastic centrifugal pump was installed adjacent to the existing river gauging station at Kingston upon Thames. The intake of the pump was located approximately 3 m from the left hand bank (looking upstream) and at a depth of 2 m below high water level (Position 2 in Figure 1). 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. A representative sample of the flow was passed continuously through the sampler, specially designed for the project by WRc. In all sampling lines and through the sampler itself, high flow velocities were maintained to avoid the settling of suspended solids.

The river discharge was measured by the Sarasota multi-path ultrasonic river gauge, operated by Thames Water at the site. Signals from the ultrasonic gauge were fed to the sample controller which activated the sampler when a specified volume of water had passed the gauging station. The sampler was thus set up to discharge 5 ml aliquots of river water into a 10 litre polypropylene container at a frequency directly proportional to the volumetric discharge of the river approximately every 5 to 10 minutes.

2.2 PRELIMINARY TESTS

Preliminary tests were carried out to assess the suitability of the sampling equipment and procedures, and the detection limits of the analytical techniques employed. The results of these tests were as follows.

- a) Recirculation experiments demonstrated that the sampling pump did not significantly affect determinand concentrations (effect $\leq 1\%$).
- b) Testing of various types of tubing material confirmed that a specific type of reinforced PVC tube was suitable for the sampling

and that it had no significant effect on the metal concentrations in the river water samples.

- c) The detection limits for the metals (defined as 3 times standard deviation of the blank) were low compared with the metal concentrations encountered in the river.
- d) Samples could be stored acidified in polyethylene bottles for a week without appreciable change in metal recovery.
- e) For the nitrate and phosphate analysis, samples required acidification to 0.01 M with sulphuric acid. Detailed experiments showed that acidification had no adverse effect upon trace metal recovery, even for lead.
- f) The detection limits for nitrate, total phosphorus and soluble reactive phosphate were low compared to the concentrations found in Thames river water.

2.3 FLOW PROPORTIONAL SAMPLING

Composite samples were collected over intervals of one week. On the day of changing the composite sample container, a grab sample of equal volume to the composite sample was taken from the outlet of the sampling pump, ie from the same sampling point as the flow-proportional samples.

The data recorded by the on-site controller during the weekly sampling routine could be printed out on an Epson FX 800 printer. The printer output included the date of the print-out, the permitted and actual number of samples obtained, and the discharge threshold used to activate the flow-proportional sampler during the sampling period. The output also showed the time at which each individual sub-sample was taken and the river flow at that time. After the data had been printed out, the controller was reset.

The proportional sampler was in place from June 1987 to December 1988.

2.4 CROSS RIVER SAMPLING

During the period when the autosampler was in operation two additional sampling exercises were undertaken to evaluate spatial variations in the concentration of different determinands and to assess whether the samples taken by the autosampler could be regarded as representative of the river cross-section as a whole (Objective 2). These exercises took place on 19 May and 30 October 1988.

As the cross sectional sampling was carried out from a single boat it was not possible for samples at different positions to be taken at exactly the same instant. It was therefore necessary to take into account the possibility of short-term temporal variations in concentration in assessing the significance of spatial differences. This temporal variation was allowed for in two ways: first, by including replication and randomisation in the design of the cross-river sampling and, second, by undertaking a further exercise specifically to estimate the temporal variation of concentration at a single sampling point over a similar time interval to that between the cross-river samples. This further exercise was carried out on 17 June 1988.

For the first cross-sectional study two sets of 2 litre grab samples were taken on 19 May 1988 from five positions across the river, points 1-5 in Figure 1. At the positions close to the bank, samples were taken at 1 m and 2 m depths and at the centre of the river at 1 m, 2 m and 3 m depths. The samples from point 2 (Figure 1) were taken from the autosampler; other samples were obtained by peristaltic pump through acid-washed tubing. The sequence of sampling from the different locations was random and selected for each set by using a die (Table 1). Average flow of the river at the time of sampling was $35.3 \text{ m}^3 \text{ s}^{-1}$.

The sampling exercise on 17 June to evaluate the temporal variations in concentration, involved taking five 2 litre grab samples directly from the autosampler at 5 minute intervals. The river discharge on this occasion was $43.0 \text{ m}^3 \text{ s}^{-1}$.

The second cross-river sampling exercise, carried out on 30 October, involved the collection of two sets of grab samples from seven locations in the river (points 1-7 in Figure 1). The samples from point 2 in this instance were taken directly from the river, not via the autosampler. Each set of samples was collected in random sequence determined with a die (Table 2). The rate of river discharge at the time of this exercise was $21.5 \text{ m}^3 \text{ s}^{-1}$.

2.5 ANALYTICAL PROCEDURES

Sampling bottles, the filtration equipment and other glass and polyethylene ware were leached in a nitric acid bath and rinsed thoroughly with double distilled deionised water prior to use. Samples were acidified on site to $0.01 \text{ M H}_2\text{SO}_4$ by addition of 5 M Analar sulphuric acid. For each composite sample the volume collected was measured in the laboratory to check that this quantity was consistent with the information printed out by the on-site data logger.

Upon return to the laboratory, samples were kept at 4°C and were analysed for Pb, Cd, Cr, Cu, Ni and Zn within 2-4 days, after preparation using the methods described in earlier reports. This involved filtration through a $0.45 \mu\text{m}$ membrane to provide a filtrate which was acidified and analysed directly. The suspended solids were digested with 1:1 concentrated nitric acid at 90°C for 2 h in Teflon digestion bombs, filtered and the filtrates diluted prior to analysis. The walls of the sampling bottles were washed with 1:1 concentrated nitric acid which was diluted and analysed. Analyses of metals were routinely carried out by GFAAS using a Perkin-Elmer Model 280 Atomic Absorption Spectrometer with HGA 400 Graphite Furnace and AS 40 Autosampler attachment with a standard additions method employed for all samples. Procedural blanks were carried out for all determinands.

Suspended solids were determined on a further aliquot of sample by filtering 1 litre of the river sample through a preweighed glass fibre paper (Whatman GF/C grade), drying the residue at 105°C and determining its weight by difference.

**Table 1 - Sequence of sample collection across the river on 19 May 1988
(see Figure 1 for position of sampling points)**

Round	Sequence	Position
I	1	1
	2	5
	3	3
	4	4
	5	2
II	6	4
	7	3
	8	1
	9	2
	10	5

Table 2 - Sequence of sample collection across the river on 30 October 1988 (see Figure 1 for position of sampling points)

Round	Sequence	Position
I	1	1
	2	3
	3	2
	4	6
	5	4
	6	5
	7	7
II	8	7
	9	5
	10	3
	11	1
	12	6
	13	2
	14	4

Nitrate and nitrite were analysed in the dissolved (GF/C filtered) fraction by ion chromatography using a Dionex 2000 i/SP chromatograph and comparison with aqueous standards. These samples were analysed also for total phosphorus (TP) and soluble reactive phosphate (SRP) following the procedures of Blair and Smith (1984).

All of the composite and grab samples for the main study were analysed for the six trace metals Pb, Cd, Cr, Cu, Ni and Zn. Determination of suspended solids started on 23 July 1987 and the non-metals, TP, SRP and nitrate were determined from 5 February 1988. The samples for the cross-sectional studies were analysed for a shorter list: Suspended solids, Pb, TP, SRP and Nitrate, with the addition of Cu for the exercise on 30 October.

2.6 TESTS FOR PRECISION OF ANALYSIS

Tests were carried out to determine the repeatability of sub-sampling, pre-treatment and analysis of the same bulk sample.

2.6.1 Trace metals

This test involved the analysis of six individual aliquots of water each derived from one large Thames river water sample before filtration. The test was performed both for dissolved and particulate matter. The blanks were analysed together with the dissolved matter and two blanks for particulate samples. The mean blank was then subtracted from the sample value. Table 3 shows the results including mean value (\bar{x}), the standard deviation (s) and relative standard deviation (RSD) for the dissolved and particulate fractions and for the fractions combined. The results show satisfactory precision within batch.

2.6.2 Total phosphorus (TP), soluble reactive phosphate (SRP) and nitrate

In the case of TP and SRP one large Thames river water sample was divided into four subsamples. Total phosphorus and soluble reactive phosphate were analysed in each sample. The results gained from this

Table 3 - Precision of pre-treatment and analysis for metals

Element	Fraction*	Subsample concentration/ $\mu\text{g l}^{-1}$						Mean	SD	RSD (%)
		S1	S2	S3	S4	S5	S6			
Zn	D	12.8	12.7	11.1	12.8	14.8	11.7	12.7	1.3	10
	P	42.0	45.5	47.0	45.0	42.0	45.0	44.4	2.0	4.5
	T	54.8	58.2	58.1	57.8	56.8	56.7	57.1	1.3	2.2
Pb	D	1.14	0.86	1.12	1.14	1.14	1.10	1.08	0.11	10
	P	2.75	2.80	2.70	2.90	2.80	2.80	2.79	0.07	2.4
	T	3.89	3.66	3.82	4.04	3.94	3.90	3.88	0.13	3.3
Cu	D	3.3	3.0	3.0	2.9	3.3	3.3	3.13	0.19	5.9
	P	3.8	3.9	4.2	3.9	4.1	3.8	3.95	0.16	4.2
	T	7.1	6.9	7.2	6.8	7.4	7.1	7.08	0.21	3.0
Cd	D	0.80	0.80	0.80	0.70	0.80	0.82	0.79	0.04	5.4
	P	0.65	0.70	0.70	0.90	0.85	0.90	0.78	0.11	14
	T	1.45	1.50	1.50	1.60	1.65	1.72	1.57	0.10	6.6
Cr	D	0.70	0.70	0.68	0.65	0.70	0.70	0.69	0.02	3.0
	P	4.0	4.2	3.8	4.1	4.1	4.0	4.03	0.14	3.4
	T	4.70	4.90	4.48	4.75	4.80	4.80	4.72	0.14	3.0
Ni	D	1.40	1.50	1.35	1.50	1.45	1.50	1.45	0.06	4.4
	P	2.70	2.70	2.55	2.70	2.50	2.70	2.64	0.09	3.5
	T	4.10	4.20	3.90	4.20	3.95	4.20	4.09	0.14	3.3

* D dissolved
P particulate
T total

test are shown in Table 4. A separate experiment was conducted for nitrate analysis. In this case one large river water sample was divided into five subsamples. The results are also included in Table 4. The relative precision of the results for all of these determinants was better than that for the trace metals.

SECTION 3 - RESULTS OF CROSS RIVER SAMPLING

3.1 SAMPLING VARIATION AT A SINGLE POINT

The results of the exercise on 17 June to determine temporal variations are shown in Table 5, where the standard deviation and relative standard deviation are measures of the variability of concentration due to the combination of short term temporal changes and analytical error. Although this variability was generally greater than variability due to analytical error alone (Tables 3 and 4) the size of increase achieves statistical significance only for Pb, Zn and TP. It should, however, be borne in mind that a more than five-fold increase in variance would be needed to achieve significance in a comparison based on the small numbers of degrees of freedom available for the metals and a more than nine-fold increase in variance for TP and SRP.

The results were sufficient to confirm that statistical analysis of the cross-river studies (described below) does need to take account of sampling variation in addition to analytical error.

3.2 VARIATION ACROSS SECTION OF RIVER

The analytical results of the cross river sampling exercises on 19 May and 30 October are set out respectively in Tables 6 and 7. For each determinant in each exercise the data were subjected to an 'analysis of variance' to address the following questions:

- a) Was there a systematic difference in concentration between rounds, ie between the first and second sets of samples taken on the same day?

Table 4 - Precision of pre-treatment and analysis of TP, SRP and Nitrate

Species	Subsample concentration					Mean	SD	RSD (%)
	S ₁	S ₂	S ₃	S ₄	S ₅			
TP/mg l ⁻¹	2.00	1.92	1.98	2.00	-	1.98	0.038	1.9
SRP/mg P l ⁻¹	1.82	1.80	1.84	1.88	-	1.84	0.034	1.9
NO ₃ /mg N l ⁻¹	34.0	34.8	33.3	34.8	34.8	34.3	0.68	2.0

Table 5 - Concentrations found in five grab samples taken directly from the autosampler at 5 minute intervals

Determinand	Grab sample concentration					Mean	SD	RSD (%)
	S ₁	S ₂	S ₃	S ₄	S ₅			
Pb/μg l ⁻¹	3.72	3.48	2.92	2.95	3.17	3.25	0.35*	11
Zn/μg l ⁻¹	48.9	48.4	42.7	42.8	36.9	43.9	4.9*	11
Cu/μg l ⁻¹	8.62	8.44	8.32	8.30	8.10	8.36	0.19	2.3
TP/mg l ⁻¹	2.16	2.08	2.28	2.28	2.00	2.16	0.12*	5.7
SRP/mg P l ⁻¹	1.92	1.72	1.88	1.90	1.90	1.86	0.08	4.4
NO ₃ /mg N l ⁻¹	7.31	6.98	6.98	6.98	6.98	7.05	0.15	2.1
TSP/ mg l ⁻¹	19.2	18.6	18.6	18.4	18.4	18.6	0.33	1.8

* Standard deviation significantly greater than sd for analytical repeatability (Tables 3 and 4)

Table 6 - Results obtained for five sampling points across the river on 19 May 1988

Sampling point (see Figure 1)	Species				
	Pb $\mu\text{g l}^{-1}$	TP mg l^{-1}	SRP mg P l^{-1}	Nitrate, mg N l^{-1}	SS mg l^{-1}
1	2.88*	1.55	1.66	6.71	18.6
	2.96**	1.37	1.57	6.36	19.2
2	3.83	1.60	1.65	7.06	19.2
	3.21	1.65	1.60	6.70	19.8
3	2.33	1.35	1.24	4.59	18.8
	2.55	1.41	1.30	6.35	19.3
4	2.94	1.39	1.30	5.65	19.7
	3.14	1.30	1.38	6.00	19.6
5	2.73	1.40	1.23	5.65	20.0
	3.39	1.45	1.35	6.00	19.8
Mean	3.00	1.45	1.43	6.11	19.4
Residual sd	0.30	0.07	0.06	0.60	0.32
Residual RSD (%)	10	4.8	4.1	9.8	1.6

* First round
 ** Second round

Table 7 - Results obtained for seven sampling points across the river on 30 October 1988

Sampling point (see Figure 1)	Species					
	Pb $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$	TP mg l^{-1}	SRP mg P l^{-1}	Nitrate mg N l^{-1}	SS mg l^{-1}
1	2.80 [*]	8.95	2.64	2.48	8.30	10.4
	2.82 ^{**}	8.69	2.60	2.48	9.26	12.0
2	2.98	9.03	2.60	2.40	8.22	10.4
	2.88	8.78	2.50	2.40	9.26	12.0
3	2.77	8.93	2.56	2.40	9.26	10.4
	2.72	9.43	2.56	2.28	9.72	10.4
4	2.85	9.03	2.60	2.48	9.26	11.2
	2.84	9.47	2.66	2.60	9.64	11.5
5	2.93	9.43	2.96	2.50	9.48	11.2
	2.79	9.08	2.76	2.64	9.54	12.0
6	2.57	9.29	2.76	2.64	9.69	9.3
	2.65	9.43	2.72	2.16	9.61	9.4
7	2.52	9.67	2.72	2.60	9.72	9.7
	2.66	9.47	2.68	2.56	9.69	9.5
Mean	2.77	9.19	2.67	2.47	9.33	10.7
Residual sd	0.065	0.23	0.065	0.14	0.41	0.65
Residual RSD %	2.3	2.5	2.4	5.7	4.4	6.1

* First round
 ** Second round

- b) Was there a systematic difference in concentration between the five (or seven) positions in the river?

From the statistical point of view a systematic difference is judged to exist if the observed difference is greater than can be accounted for by the variability associated with sampling and chemical analysis. This variability is measured by the residual standard deviation, as given in Tables 6 and 7. The outcomes of the analyses of variance are summarised in the first two pairs of rows in Table 8.

For none of the data sets was there a significant difference between rounds. The interpretation of this is that there were no systematic time-trends in concentration throughout the duration of the exercise on 19 May, nor on 30 October.

The analyses of variance did reveal some differences between positions that would be difficult to ascribe to sampling variation alone. On 19 May the concentrations for SRP were higher at sampling points 1 and 2 near to the left-hand bank than at 3, 4 or 5 in mid-stream (see Table 6). Disparities of this size could have arisen by chance less frequently than once in 200 similar studies. This result was one of the reasons why the second exercise was carried out.

On the second occasion, 30 October, there was no significant variation for SRP and no confirmation of the difference previously observed. There was a significant difference between positions for TP, but this could be attributed to a single high sample value (Position 5 Round 1) from which a strong conclusion should not be drawn.

On 30 October there were significant differences between positions for Pb and SS. In each of these cases the concentrations were systematically lower at sampling points 6 and 7, near to the right hand bank, by about 10% of the overall mean.

The results of the two exercises are generally reassuring that heterogeneity of concentration across the section of this river is not a

Table 8 - Summary of cross river analyses for (a) 19 May and (b) 30 October

		Pb	Cu	TP	SRP	Nitrate	SS
Was there a systematic difference between rounds?	(a)	No	-	No	No	No	No
	(b)	No	No	No	No	No	No
Was there a systematic difference between sites?	(a)	No	-	No	Yes	No	No
	(b)	Yes	No	Yes	No	No	Yes
Least significant difference between sites	(a)	0.78	-	0.18	0.15	1.50	0.82
	(b)	0.15	0.55	0.15	0.34	0.97	1.5
As % of mean	(a)	26	-	12	11	25	4
	(b)	6	6	6	14	10	14
Least significant difference between bank and centre	(a)	0.50	-	0.12	0.10	1.0	0.53
	(b)	0.10	0.35	0.10	0.22	0.63	1.0
As % of mean	(a)	17	-	8	7	16	3
	(b)	4	4	4	9	6	9

* expressed in same units as in Tables 6 and 7

serious problem. The largest difference (for SRP on 19 May), amounting to 25% of the mid-stream concentration, was not observed consistently between the two exercises. However, in any study of this type it is important to bear in mind that genuine systematic differences can go undetected because they fail to show above the 'noise' in the measurements. The theoretical 'least significant differences' are set out in Table 8. These are the sizes of the smallest differences that would have been declared as significant, if they had been observed. These figures convey an idea of the power and the limitations of these studies.

It may be noted that the residual standard deviation for Pb was much lower on 30 October than it had been on 19 May and, indeed, lower than the standard deviation observed in the investigation of temporal variability on 17 June (Table 5). As these standard deviations are each measuring short-term sampling variation, plus analytical error, they would be expected to be of similar size. The reason for the improvement is not known.

SECTION 4 - ESTIMATION OF LOAD

4.1 AVAILABLE DATA

The full set of composite and grab sample concentrations, together with the respective measurements of flow are given in Appendices A and B. These include information on 55 time intervals. For the following comparative studies only those observations were included for which the composite sample represented a full seven-day operating period. Data were then available for:

48 weeks for trace metals
42 weeks for suspended solids
30 weeks for TP, SRP and nitrate.

The comparisons of load estimates presented later in this report should be regarded as referring to the periods of time defined by these sets of data. The additional data available but not used for the load calculations are indicated in Appendices A and B.

4.2 COMPARISON OF METHODS

The comparison of estimates of load based on discrete samples with those based on continuous flow-proportional sampling is more difficult than might at first appear, because it involves two questions of a statistical nature.

- i) By what method of calculation should the grab sample concentrations and their associated flow measurements be combined? There is more than one possibility.
- ii) Can the reliability of the estimates be quantified (in terms of standard errors or confidence intervals)? If so, this should enable more general conclusions to be drawn about the relative merits of the different methods than would be possible from individual values.

The full technical discussion of these questions is beyond the scope of the present report. In this study the estimates of load calculated from continuous sampling (we call this Method 1) were used as a base point for comparison with two different methods of operating with the discrete sample data. These methods, which we denote as Methods 2 and 3, are the same as those referred to by Walling and Webb (1985) as their Methods 5 and 2 respectively. The three other methods considered by Walling and Webb were shown to be appreciably biased and so have not been further examined.

4.3 DETAILS OF THE METHODS

To enable description and discussion of the methods it is helpful to have some mathematical notation and definitions of terms.

In this report 'load' is taken to mean the rate of transfer of mass of substance past the measurement station. This term is used, with appropriate qualification, to refer either to the rate of transfer at a given instant or to the average rate over a period. The comparisons of method are concerned with the estimation of the mean load discharged over the period of the study.

The period of time over which the study took place can be thought of as comprising n intervals each of one week in length. Using i as an index taking values from 1 to n , let:

t_i be the date of sample collection at the end of the i th interval,

C_i the concentration of substance in the flow-proportional composite over the i th interval,

Q_i the average flow during the i th interval,

$\bar{Q} = \sum_{i=1}^n Q_i / n$, the average flow over the whole period,

c_i the grab sample concentration at time t_i ,

q_i the instantaneous flow at time t_i ,

$l_i = c_i q_i$, the instantaneous load at time t_i ,

$\bar{q} = \sum_{i=1}^n q_i / n$, the average of the instantaneous measurements of flow,

$\bar{l} = \sum_{i=1}^n l_i / n$, the average of the instantaneous measurements of load, and

$\bar{c}_w = \bar{l} / \bar{q}$, the flow-weighted average concentration of the grab samples.

Method 1

Using the concentrations measured in the flow-proportional composite samples, together with average flows derived from continuous measurement, it is possible to calculate the average load,

$$M_1 = \sum_{i=1}^n C_i Q_i / n.$$

There should be negligible error in this estimate arising from temporal variability of concentration or of flow as these variations have already been integrated into C_i and Q_i . With regard to the problem of taking these variations into account, this method provides the 'right' answer. The value of M_1 will be subject to other uncertainties arising from:

analytical errors,
errors in the measurement of flow,
imperfect mixing across the section of the river.

With methods of analysis that are as precise as those used in the present study the impact of analytical error on the estimate of M_1 is likely to be very small, since the formula is a weighted average of n determinations. The size of systematic error that might arise from imperfect mixing is discussed in Section 6. Error in the measurement of flow is a possibility that needs to be considered and this would affect all of the methods of load estimation considered here.

Method 2

Where there is available a continuous record of flow, but concentrations derived only from grab samples, a popular method of estimating load is to take the arithmetic mean of the instantaneous loads and adjust it for mean flow over the period of the record. In this method the average load is estimated by

$$M_2 = \bar{1} \bar{Q} / \bar{q}$$

$$= \bar{c}_v \bar{Q},$$

these being identically equivalent modes of expression.

The adjustment in this formula for the difference between \bar{q} and \bar{Q} has intuitive appeal but the theoretical evaluation of the operating

characteristics of the resulting equation is not very easy. Although, for this purpose, it would be legitimate to regard \bar{Q} as a constant, both the grab concentrations c_1, \dots, c_n and the instantaneous flows q_1, \dots, q_n need to be treated as subject to statistical variation.

With regard to possible bias, it is straightforward to show that the expected value of this estimator satisfies the relationship,

$$E(M_2) = E(\bar{l}) - \text{cov}(\bar{c}_w, \bar{q}),$$

where $E(\bar{l})$ is the expected value of average load and the final term represents the covariance of \bar{c}_w and \bar{q} . This last term is mathematically difficult to analyse but examples may easily be constructed to show that in general it will not be equal to zero. At a rough approximation it would appear that this term behaves rather like

$$\text{cov}(c_i, q_i)/n$$

and so its size is inversely proportional to n . Estimates of $\text{cov}(c_i, q_i)$ in comparison with $E(\bar{l})$ are given in Appendix C for the different determinands included in this study.

The consequences of all this are that Method 2 can, in general, be subject to bias although the size of the bias diminishes with increasing n . It will be seen later from the results in Section 4.3 and Appendix C that, in the situation studied at Kingston, this bias would be negligible in comparison with other sources of error.

With regard to the repeatability of estimation based on discrete sampling in conjunction with Method 2, an approximate formula for the standard error of \bar{c}_w was given by Jolly (1986). This has hitherto been used by WRc for calculating confidence intervals associated with Method 2. The derivation of that formula was, however, approximate in that it paid greater attention to the variability of c_i than that of q_i . Although limited simulation exercises have confirmed the validity of the formula, we now prefer another approach to derive confidence limits for M_2 in a way that is closer to standard statistical theory.

The estimator for Method 2 is essentially a quotient of the averages \bar{l} and \bar{q} . In order to give a confidence interval for this, the method of Fieller as explained by Kendall and Stuart (1979) can be used and this is the method that has been adopted in the present report. However for readers who wish to see the effect of this change, comparative results from the two methods are set out in Appendix D.

It is important to note that there are circumstances when Fieller's method will not work, in particular when

$$\bar{q}^2 < t_{\alpha} SE(\bar{q})^2$$

where $SE(\bar{q})$ is the estimated standard error of \bar{q} and t_{α} is the value of Student's t for the appropriate tail probability α . These circumstances, however, correspond to ones in which the reliability of estimates based on grab sampling will be hopeless, because of too few observations in relation to the variability in flow.

Method 3

Using only the instantaneous measurements there is the simpler unadjusted formula

$$M_3 = \bar{l}$$

which estimates the mean load over the period as the straightforward average of the instantaneous loads. If these are viewed as a simple random sample from the statistical distribution of instantaneous loads, then M_3 is unbiased and its standard error would be given by

$$SE(M_3) = s/\sqrt{n}$$

where s is the sample standard deviation of the loads l_i . A confidence interval for M_3 may then be calculated in the usual way. In the present study, if the mathematical formula for the lower confidence limit yielded a negative number, the lower limit was taken to be zero.

4.4 STATISTICAL ASSUMPTIONS AND RESERVATIONS

It is important to draw attention to two statistical assumptions that underlie the theoretical discussion of Methods 2 and 3 in Section 4.3 but which in practice are likely to be only imperfectly satisfied.

The first is the assumption that the n instantaneous measurements of concentration, flow and hence load can be regarded as random, independent and identically distributed observations from their respective populations. This assumption can not be quite correct since the times of the observations were evenly spaced, while the variations in flow and concentration almost certainly contained some systematic components. This being so, the formulae used to calculate confidence limits would tend to give intervals that are wider than necessary. This cannot, however, be demonstrated convincingly without much more intensive sampling (Ellis and Lacey 1980).

The second assumption is that the average values \bar{q} and \bar{l} can be regarded as if they were normally distributed. This would definitely be untrue of the individual measurements, q_i and l_i , but often it is possible to rely on 'central limiting' behaviour to ensure approximate normality of averages, even for quite modest numbers of samples. However, in the present application, the distributions of flow and load are so highly skew that the assumption of normality of the averages must be regarded as doubtful. This diminishes the validity of the confidence limits for all the procedures so far discussed and would point to the need to consider more complicated alternatives.

The problems posed by both of the above reservations could be subjects of further study, although, if continuous monitoring is adopted, these difficulties simply do not arise.

4.5 RESULTS OF COMPARISON

Calculations were undertaken to enable comparison of the three methods of estimation of the average loads discharged over the period of the

study. For the trace metals, weekly loads and 95% confidence limits for methods M_2 and M_3 were based on the following sampling frequencies: 48, 24, 12 and 6, representing samples taken weekly, fortnightly, monthly and bimonthly. For suspended solids, the numbers of grab samples considered were 40, 20 and 10 and for TP, SRP and $\text{NO}_3\text{-N}$, there were 30, 15 or 8 samples, corresponding to weekly, fortnightly or monthly sampling respectively. In all cases the subsets of grab samples were selected by stepping in regular intervals from the first available date of sampling. This is, of course, not the only method by which subsets could have been selected but it does provide realistic examples of what would happen in practice if lower rates of sampling are used.

The results of these calculations are presented in Table 9 and in graphical form in Figures 2-11.

In this particular set of results there was a tendency for the load estimates based on continuous monitoring (Method 1) to be larger than those based on the discrete samples (Methods 2 or 3). This is true for most but not all determinands. It would, however, be incorrect to draw a general conclusion from this pattern, since the results for different determinands are not statistically independent. The results are all derived from the same set of sampling dates; if these had been different, a different general pattern might well have been seen.

The confidence limits for M_3 straddle the value of M_1 in most cases, confirming that the results of these methods are consistent with each other. Although the confidence limits for M_2 fail to include the value of M_1 in a number of cases, the sizes of the disparities are not large enough to force the conclusion that M_1 and M_2 are inconsistent. They do, however, confirm that the confidence intervals for M_2 are not over-stating the possible inaccuracies associated with that method.

As would be expected, the precision of the load estimated by Methods 2 and 3 improves with sample frequency as indicated by the confidence intervals. For most of the data sets the confidence interval for Method 3 is wider than that for Method 2, but it is possible that this

Table 9 - Load estimates (tonnes per week) with 95% confidence limits for weekly, fortnightly, monthly and bimonthly frequency of sampling, compared with estimates based on composite measurement

		Mean	Lower	Upper			Mean	Lower	Upper
Cd					Cr				
Composite	M1	0.055			M1	0.194			
Weekly grab	M2	0.044	0.036	0.054	M2	0.160	0.130	0.184	
	M3	0.043	0.030	0.056	M3	0.156	0.093	0.219	
Fortnightly grab	M2	0.041	0.030	0.057	M2	0.150	0.096	0.182	
	M3	0.041	0.022	0.061	M3	0.151	0.056	0.247	
Monthly grab	M2	0.046	0.016	0.066	M2	0.144	0.032	0.225	
	M3	0.039	0.008	0.071	M3	0.123	0.016	0.231	
Bimonthly grab	M2	0.035	0.012	0.076	M2	0.090	0.065	0.226	
	M3	0.033	0.007	0.059	M3	0.084	0.053	0.116	
Cu					Pb				
Composite	M1	0.351			M1	0.188			
Weekly grab	M2	0.292	0.265	0.321	M2	0.152	0.108	0.186	
	M3	0.284	0.196	0.371	M3	0.148	0.080	0.216	
Fortnightly grab	M2	0.291	0.253	0.343	M2	0.151	0.071	0.195	
	M3	0.294	0.159	0.429	M3	0.153	0.041	0.265	
Monthly grab	M2	0.321	0.217	0.371	M2	0.140	0.083	0.208	
	M3	0.275	0.088	0.462	M3	0.120	0.045	0.196	
Bimonthly grab	M2	0.344	0.152	0.413	M2	0.180	0.065	0.253	
	M3	0.323	0.044	0.602	M3	0.169	0.022	0.316	
Ni					Zn				
Composite	M1	0.244			M1	1.69			
Weekly grab	M2	0.188	0.145	0.247	M2	1.51	1.36	1.62	
	M3	0.183	0.130	0.236	M3	1.47	0.94	2.00	
Fortnightly grab	M2	0.180	0.129	0.292	M2	1.51	1.29	1.64	
	M3	0.182	0.123	0.241	M3	1.53	0.70	2.35	

Table 9 - Continued

		Mean	Lower	Upper			Mean	Lower	Upper
Ni					Zn				
Monthly grab	M2	0.206	0.164	0.258	M2	1.62	1.10	1.84	
	M3	0.176	0.078	0.275	M3	1.39	0.44	2.34	
Bimonthly grab	M2	0.226	0.151	0.291	M2	1.60	0.80	2.01	
	M3	0.212	0.049	0.375	M3	1.51	0.24	2.77	
SS					TP				
Composite	M1	1090			M1	52			
Weekly grab	M2	870	430	1140	M2	52	43	69	
	M3	880	310	1460	M3	54	40	67	
Fortnightly grab	M2	990	0	1430	M2	48	37	96	
	M3	1040	0	2150	M3	55	35	74	
Monthly grab	M2	740	0	1130	M2	42	*	*	
	M3	650	0	1340	M3	61	22	100	
Bimonthly grab	M2	900	0	1450	M2	40	*	*	
	M3	800	0	2360	M3	77	0	178	
SRP					NO3				
Composite	M1	44			M1	528			
Weekly grab	M2	46	37	66	M2	354	156	565	
	M3	48	39	57	M3	369	130	607	
Fortnightly grab	M2	44	32	100	M2	267	192	293	
	M3	51	36	65	M3	306	76	536	
Monthly grab	M2	38	*	*	M2	280	*	*	
	M3	55	28	82	M3	410	0	870	
Bimonthly grab	M2	32	*	*	M2	296	*	*	
	M3	61	0	126	M3	574	0	1795	

* Confidence limits not calculable by Fieller's method
See text: Sections 4.3 and 4.5

is a reflection of the approximations used in their respective formulae rather than an indication of a true superiority of one method over the other.

It is noted in Table 9 that for the two lowest sampling frequencies for TP, SRP and nitrate the method based on Fieller's theorem was unable to provide finite confidence limits. The confidence intervals have not therefore been shown in Figures 9, 10 and 11, although they could be regarded as stretching from zero to infinity!

SECTION 5 - RELATIONSHIPS BETWEEN CONCENTRATIONS, FLOW AND SUSPENDED SOLIDS

5.1 CONCENTRATIONS AND FLOW

For each determinand in turn, Figures 12 to 15 illustrate the relationship between grab sample concentration and instantaneous flow rate and Figures 16 to 19 that between composite sample concentration and average flow. These show several distinct patterns, which tend to be more pronounced for the composite samples:

- i) Suspended solid concentrations are constant (with appreciable scatter) below $\sim 80 \text{ m}^3 \text{ s}^{-1}$ discharge. Above this flow rate resuspension processes become significant and the concentration rises with flow rate.
- ii) Total phosphate and soluble reactive phosphate decrease with discharge for flows below $\sim 150 \text{ m}^3 \text{ s}^{-1}$ and then stabilise. This suggests a relative constant input with the concentrations being influenced by dilution as the discharge increases.
- iii) Nitrate shows no obvious increase or decrease with discharge. This might be consistent with the main contribution of the nitrate in the river being derived from run-off with the concentration in the run-off being independent of the volume.

- iv) Trace metals tend to show a U-shaped curve, with a minimum at $70-100 \text{ m}^3 \text{ s}^{-1}$. This can be interpreted as indicating that the concentration for low flows in the range of $0-80 \text{ m}^3 \text{ s}^{-1}$ is affected by dilution processes and that resuspension of metal-rich sediments contributes to the increase at high flows.

5.2 CONCENTRATIONS AND SUSPENDED SOLIDS

Figures 20 to 28 illustrate the relationships between the concentrations of other determinands and those of suspended solids.

In general the correlations between these pairs of variates were poor, offering no hope of predictive modelling. The only exceptions where correlations achieved any degree of significance were TP and SRP but these were almost certainly a simple reflection of the earlier observed relationships between TP and SRP and flow.

These results give discouragement to any idea that suspended solids might be a useful surrogate parameter for predicting the concentrations of other determinands in circumstances where the latter have not been analysed.

SECTION 6 - DISCUSSION

There are a number of sources of error or uncertainty that may limit the accuracy of estimation of the loads of pollutants carried by rivers to the sea. If we restrict attention to the problem of estimating the load which passes a given flow-gauging point, it is necessary to consider:

- a) errors in analytical determination of concentration;
- b) errors in measurement of flow;
- c) heterogeneity of concentrations across the section of the river;

- d) the effects of temporal variations in concentration and flow if the monitoring of either of these quantities is not continuous through time.

The present study was undertaken particularly to investigate (d) by providing a bench-mark based on continuous monitoring, against which the accuracy of methods based on grab sampling could be compared. The study also included exercises to quantify the effects of (a) and (c). The accuracy of measurements of flow has been studied elsewhere and was not reconsidered.

Using analytical methods similar to those in this study the analytical error on an individual sample determination is unlikely to exceed 5-10% (double the RSD in Tables 3 and 4). The impact of errors of this size on estimates of load is going to be very small, because of the effect of averaging. In calculating an annual mean based on, say, 24 samples, the uncertainty due to this source of error would be at most 1 or 2%.

Errors of measurement of flow have not been considered in this study but in as far as such errors are random they are likely to be averaged out in much the same way as errors of analysis. There could, however, also be systematic error in the measurement of flow of about $\pm 5\%$, which would affect both instantaneous and continuous measurements.

Systematic differences in concentration across the section of river at Kingston upon Thames do not appear to raise a serious problem. The study did not reveal strong evidence for the existence of such trends but from the limited scale of the investigation it would be safe to conclude only that if such differences do exist they are unlikely to be greater than 20% of the mean cross-sectional concentration. The effect that such differences might have on the estimation of average loads would unlikely be larger than $\pm 10\%$.

The errors in load estimation when loads are estimated from a relatively small number of grab samples can be much larger than those due to (a), (b) or (c). This is shown by the results in Table 9 and Figures 2 to 11

which confirm that the confidence limits, associated with Method 3 and with Method 2, are not over-cautious but provide a realistic measure of the uncertainty associated with load estimates obtained from grab samples.

It is not possible from the results of this work to draw a firm conclusion about the relative merits of the two alternative ways of calculating loads from grab sample data (Methods 2 and 3). Method 2 may have intuitive appeal but leads to more difficult statistical analysis than Method 3. Although this report offers more satisfactory solutions to the questions of bias and precision than had previously been given (Jolly 1986), the calculations that are involved are not simple. They may leave the reader wondering whether all this trouble provides a worthwhile advantage over the much more straightforward Method 3. The last word on this has not yet been said but, in the meantime, it must be recognised that for neither method can statistical theory provide a complete safeguard against the hazards of sampling at only a discrete set of instants.

The results of this study are based on measurements taken at a single station, on a particular river and over a limited period of time. Any generalisation of the conclusions to a wider set of circumstances would rest on informal judgements about whether the conditions at Kingston upon Thames in 1987-88 can be regarded as more or less typical of those which might be encountered elsewhere. With regard to the question of heterogeneity across the section of the river, the Thames would appear to offer as good a test as is possible in the UK, since the river is relatively wide and slow. However, with regard to the errors in load estimation that are associated with discrete sampling, the Thames is unlikely to be a 'worst case', since many other rivers exhibit more extreme flow variations.

SECTION 7 - CONCLUSIONS

1. A method of load estimation based on continuous flow measurement and flow-proportional sampling has been demonstrated to be feasible. It offers an accurate method for estimating loads.
2. At Kingston upon Thames, the river was well enough mixed (in cross-section) for a single sampling point to be representative of the total flow. The possible error in load estimation arising from incomplete mixing is judged to be smaller than $\pm 10\%$.
3. Comparisons between the traditional methods of load estimation based on grab sampling, and the results from the system of continuous monitoring showed that the results are generally statistically consistent but that the estimates based on grab samples suffer from large inaccuracies due to their failure to account fully for variations in concentration and flow.
4. As a broad generalisation, estimates of annual load based on weekly grab sampling are accurate only to within $\pm 25\%$, while estimates based on monthly grab samples could easily err by as much as $\pm 50\%$.
5. The effects of analytical errors and of errors in flow measurement are likely to be of much less practical importance than the inaccuracies due to discontinuous measurement.

ACKNOWLEDGEMENT

The University of Essex and the Water Research Centre thank Thames Water for its help and facilities made available for this research.

REFERENCES

- BLAIR A J and SMITH P R (1984) The Determination of Low Level Soluble Reactive Phosphate in Surface Waters using an Autoanalyzer II and Total Phosphorus by Pre-Digestion in an Autoclave. WRc Report 799-M.
- ELLIS J C and LACEY R F (1980) Sampling: defining the task and planning the scheme. Journal of the Institute of Water Pollution Control 79(4), 452-467.
- JOLLY P K (1986) Estimates of the Loads of Certain List I and List II Substances Discharged to the North Sea. WRc Report 1350-M/1.
- KENDALL M and STUART A (1979) The Advanced Theory of Statistics, Volume 2 (Fourth Edition). Griffin, London and High Wycombe, Example 20.7 p136-138.
- 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.

Figure 1. Location of sampling points across the River Thames at Kingston upon Thames

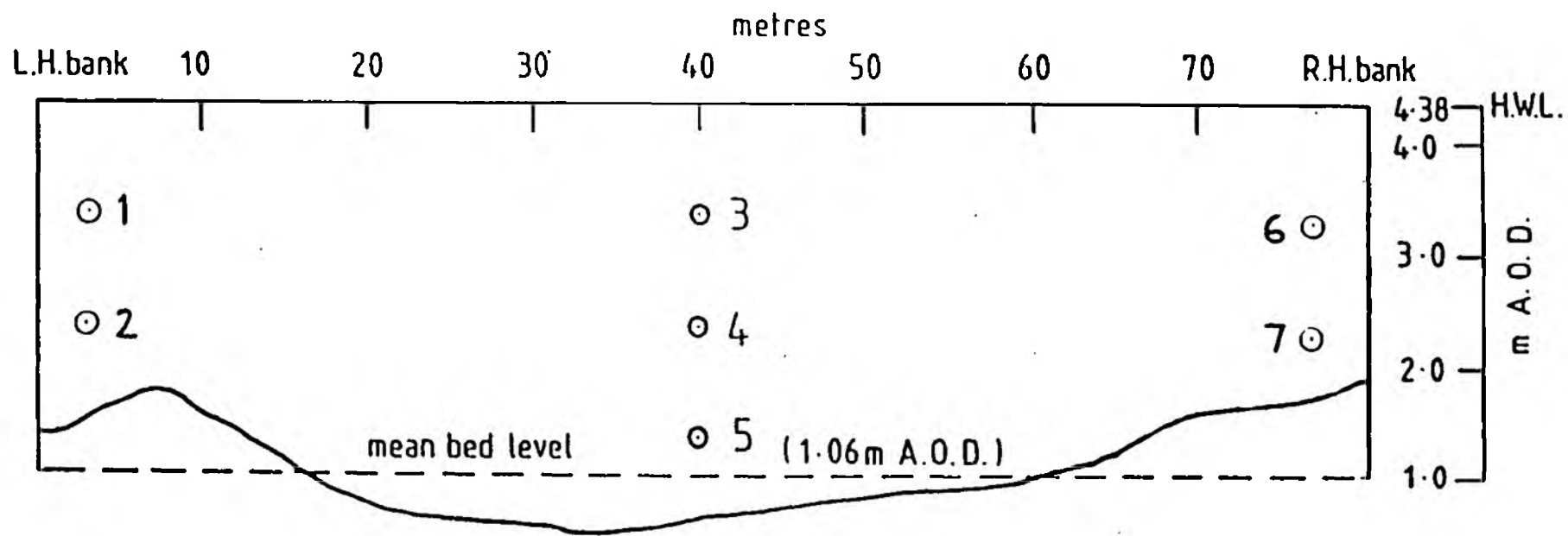


Fig.2: Load Estimates (Tonnes/Week) with 95% confidence limits
Cd

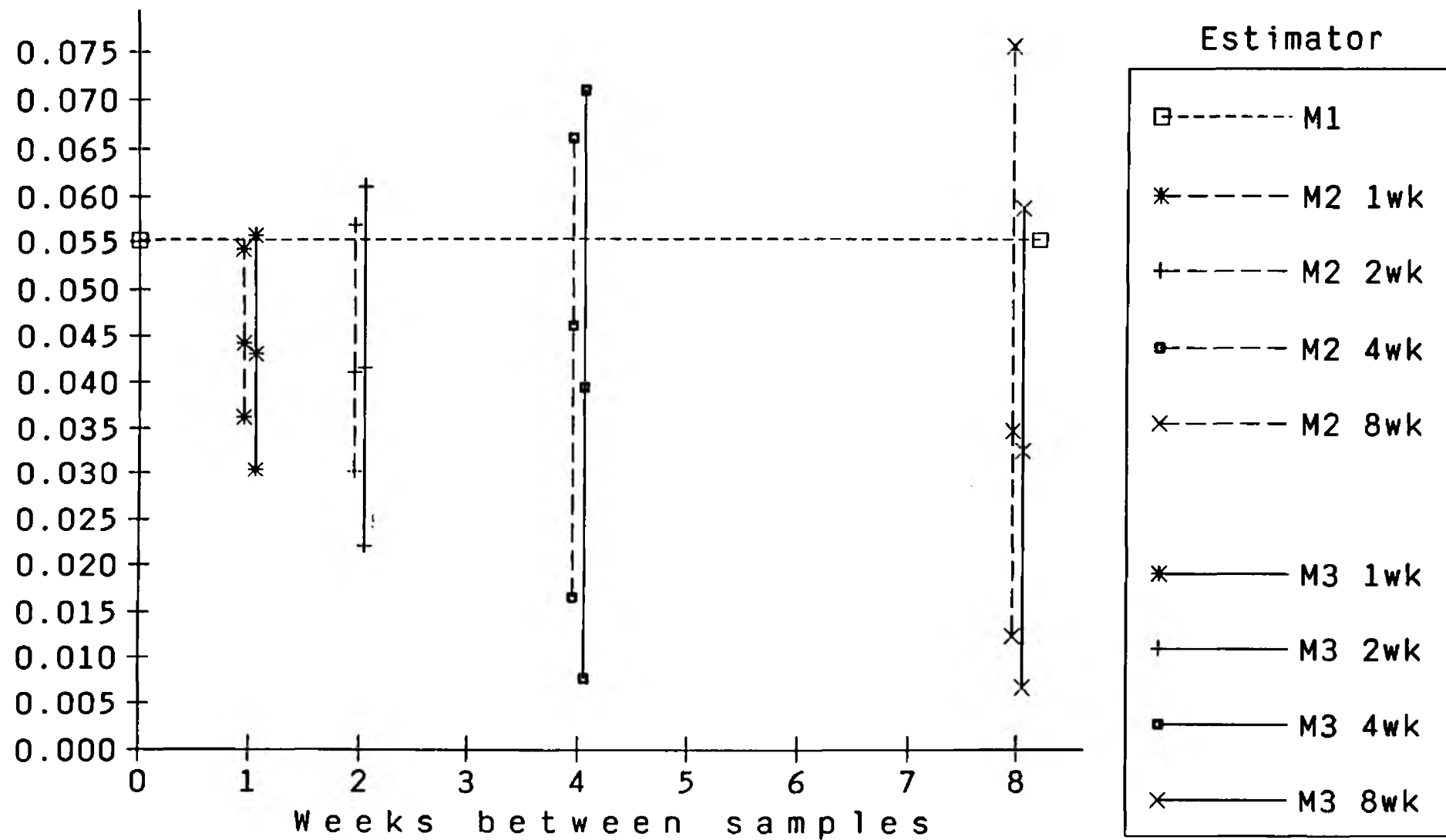


Fig.3: Load Estimates (Tonnes/Week) with 95% confidence limits
Cr

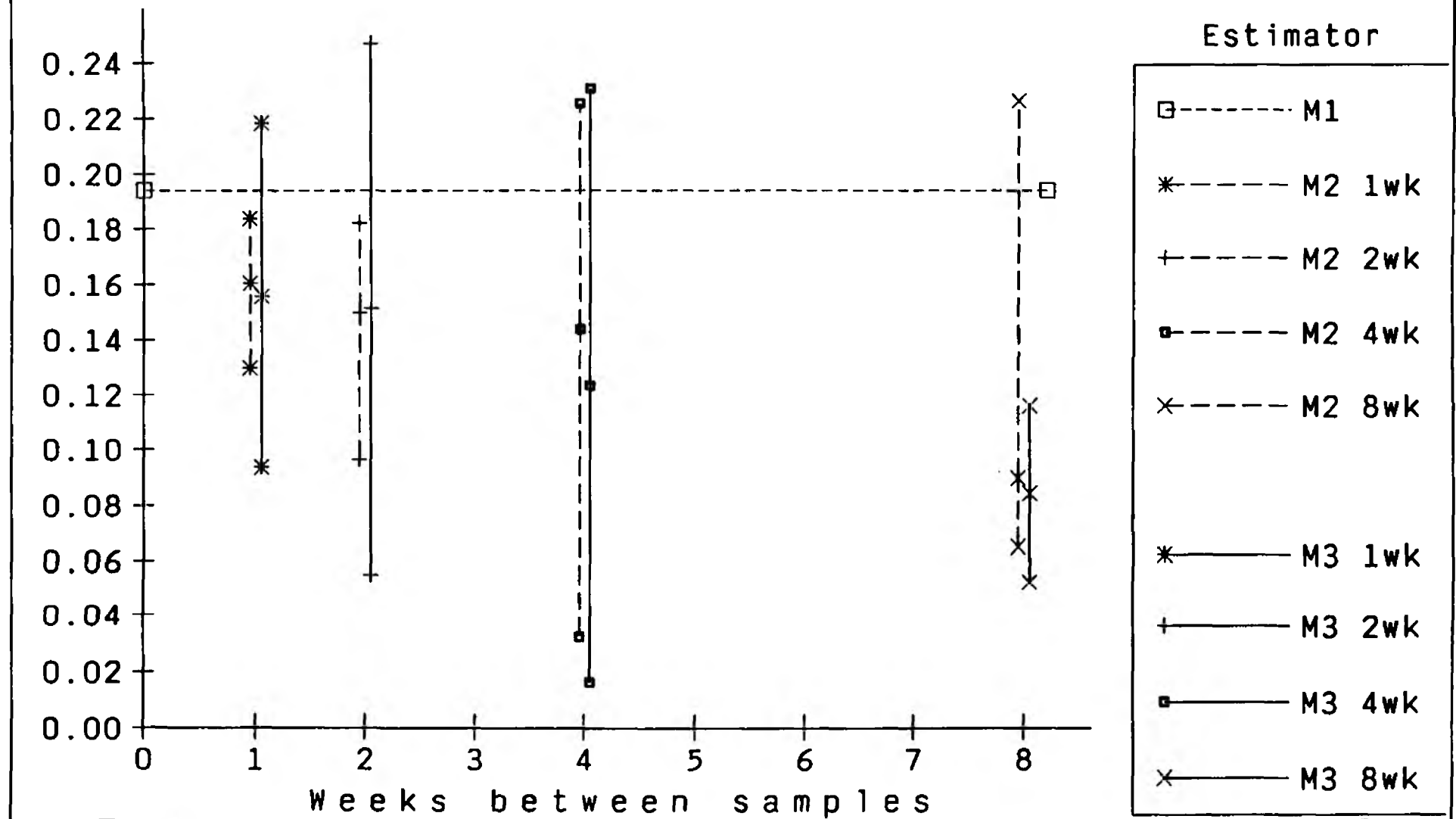


Fig.4: Load Estimates (Tonnes/Week) with 95% confidence limits
Cu

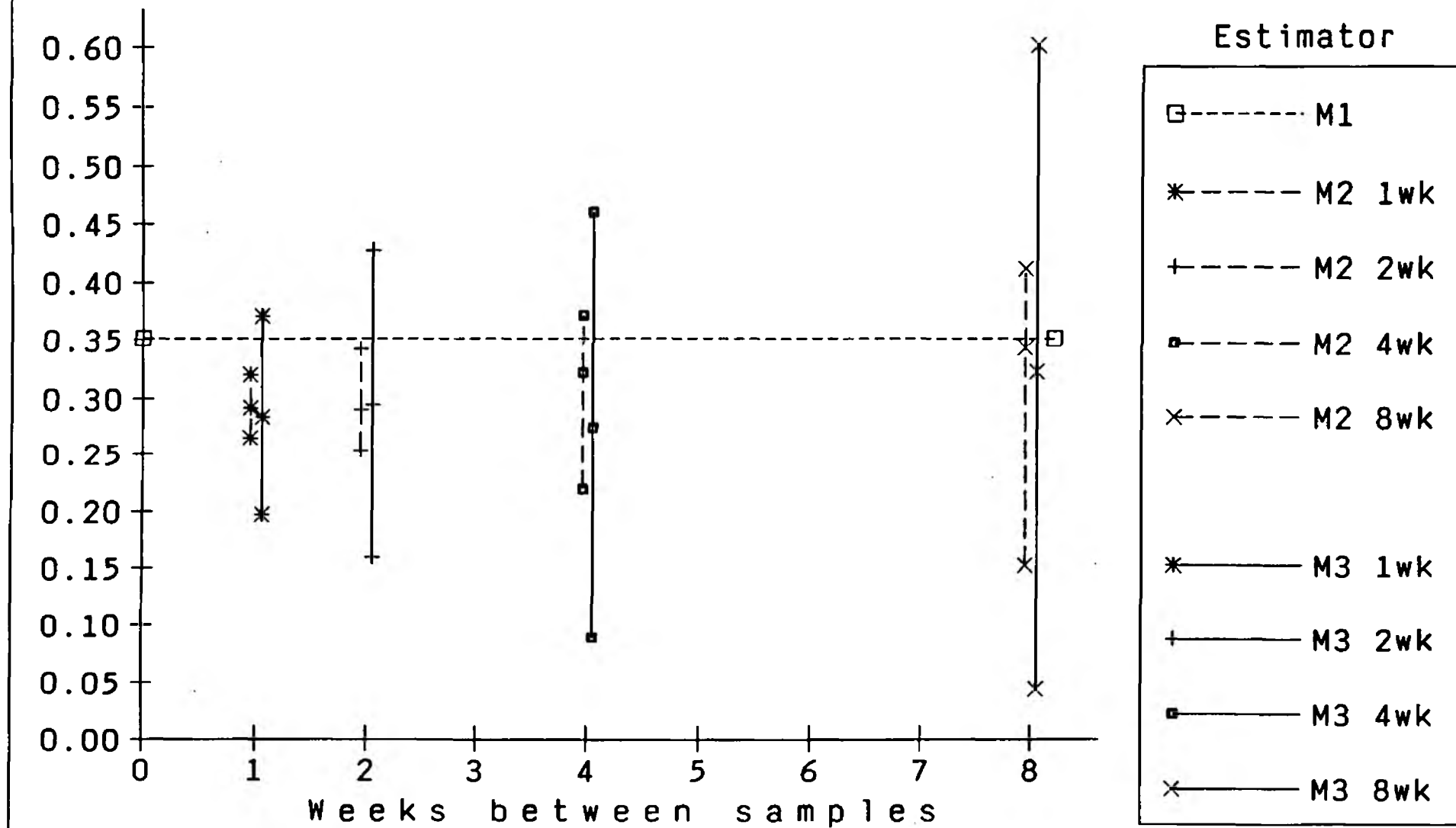


Fig.5: Load Estimates (Tonnes/Week) with 95% confidence limits
Pb

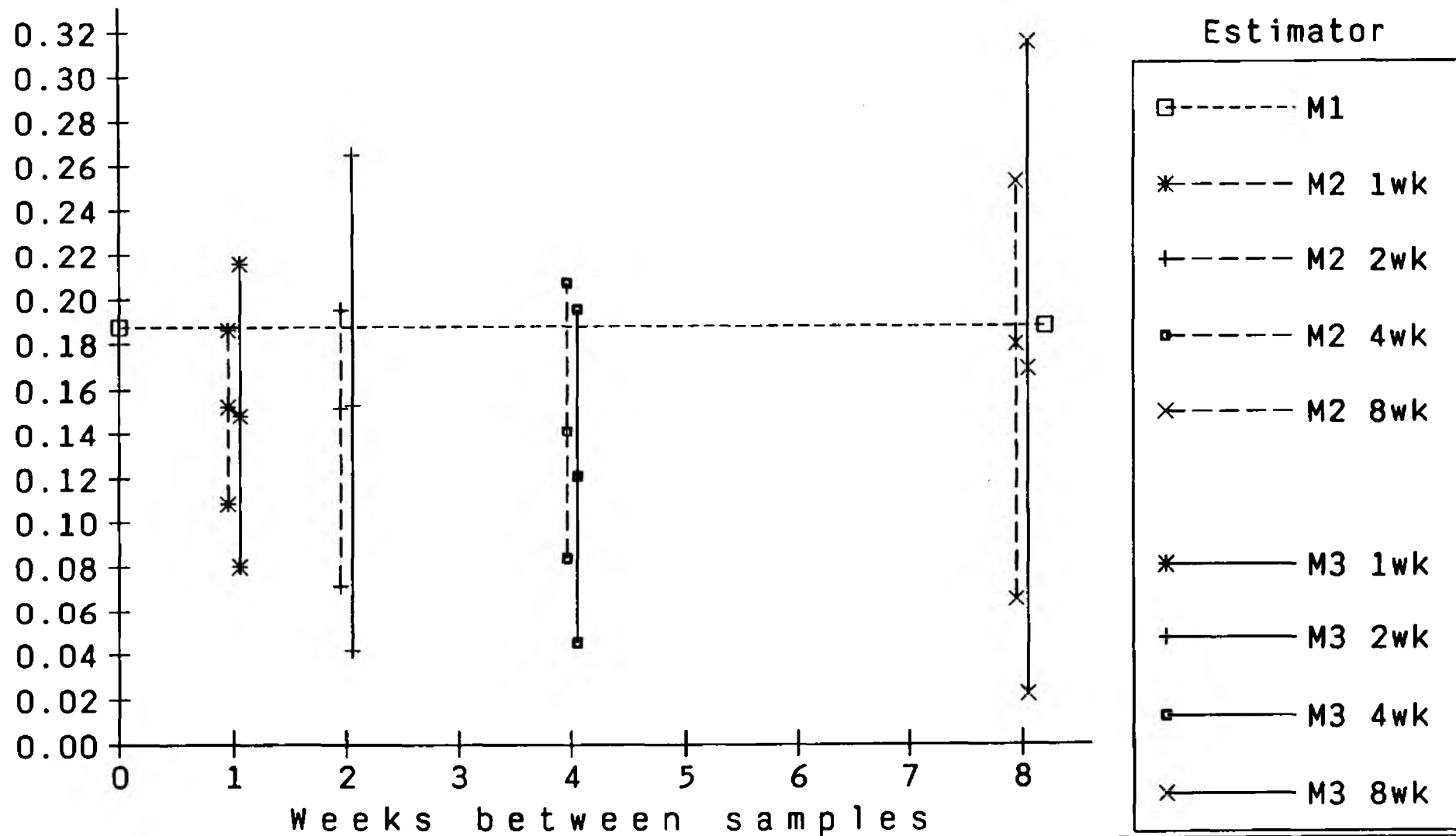


Fig.6: Load Estimates (Tonnes/Week) with 95% confidence limits
Ni

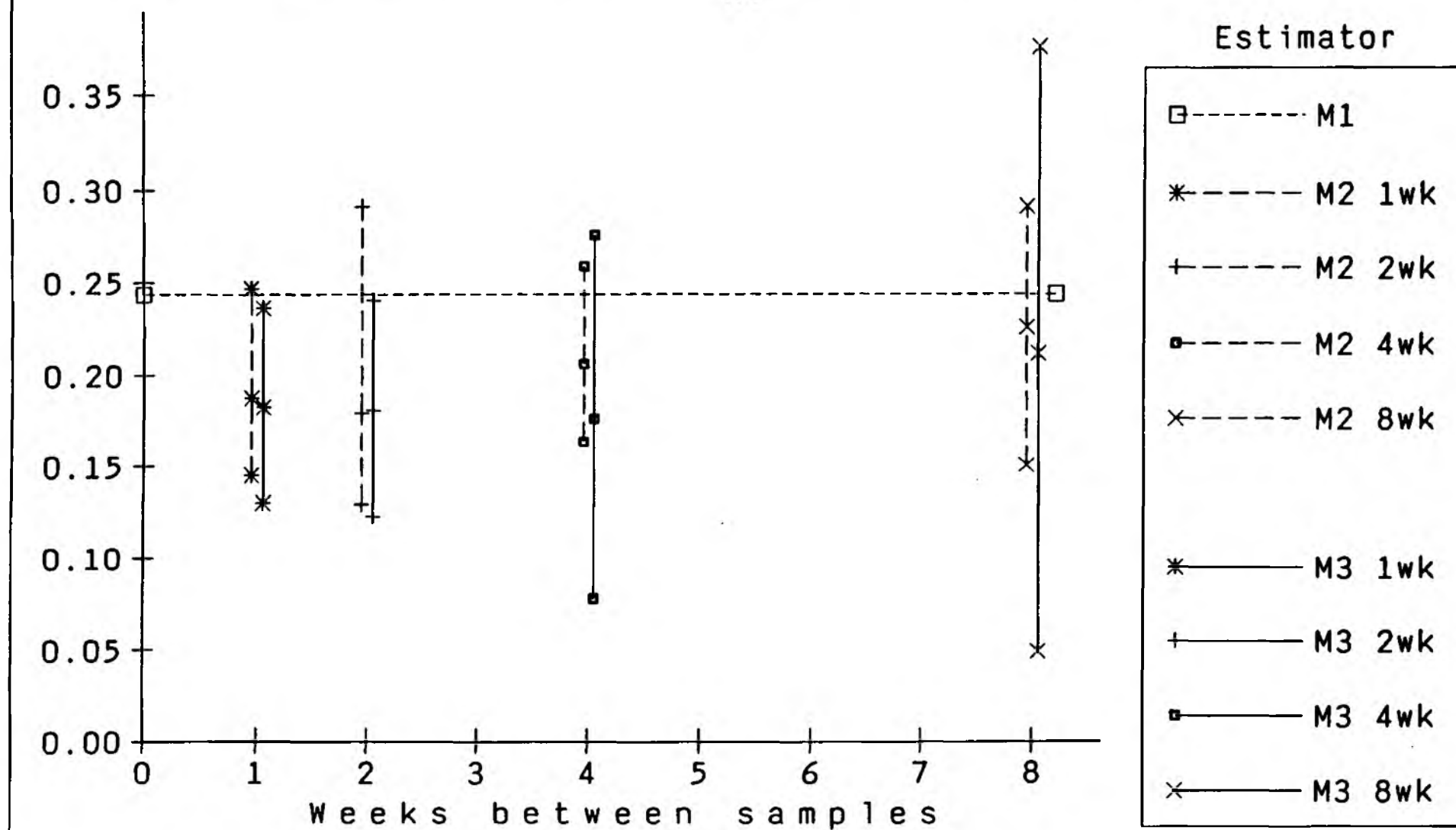


Fig.7: Load Estimates (Tonnes/Week) with 95% confidence limits
Zn

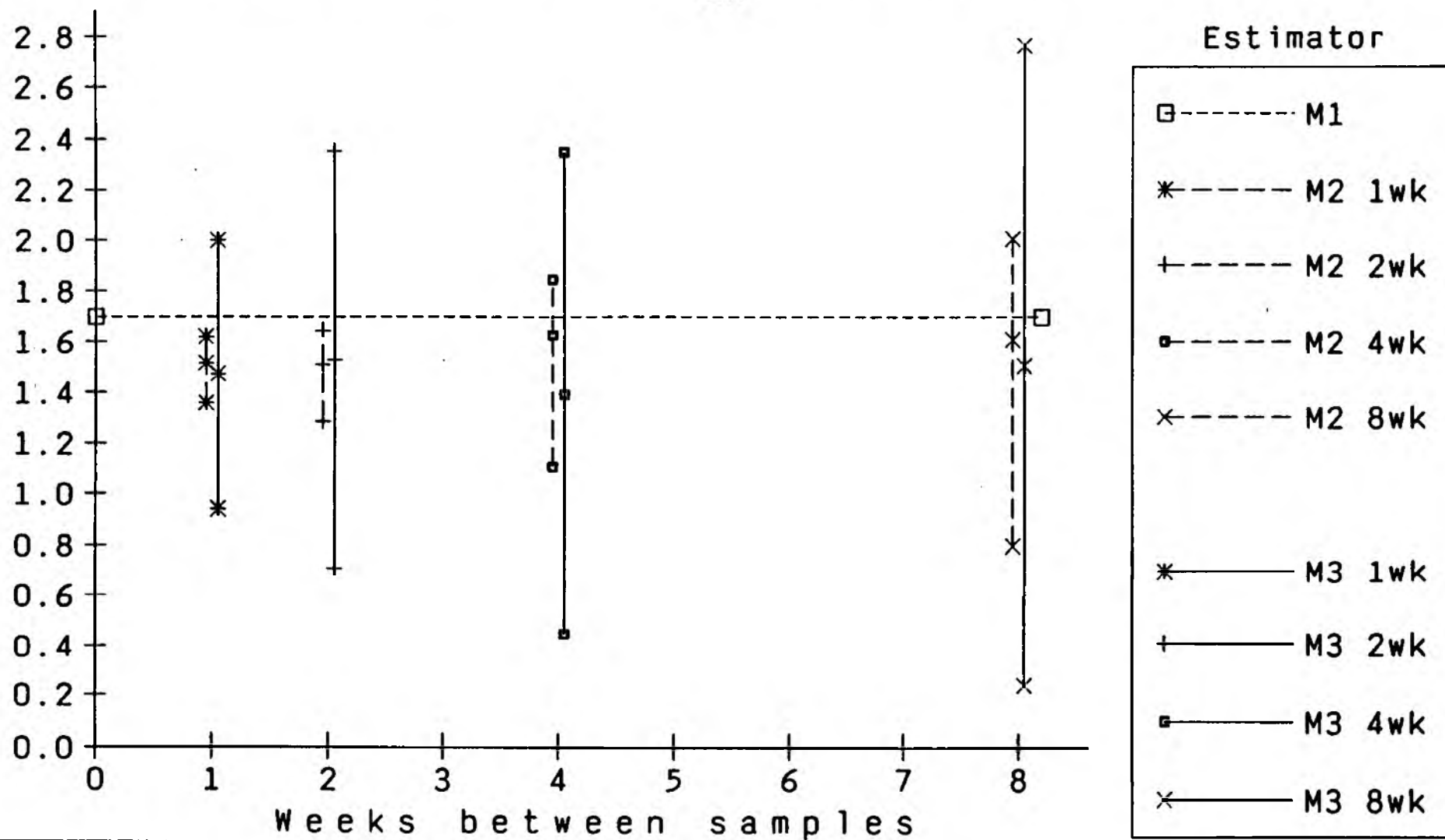


Fig.8: Load Estimates (Tonnes/Week) with 95% confidence limits
SS

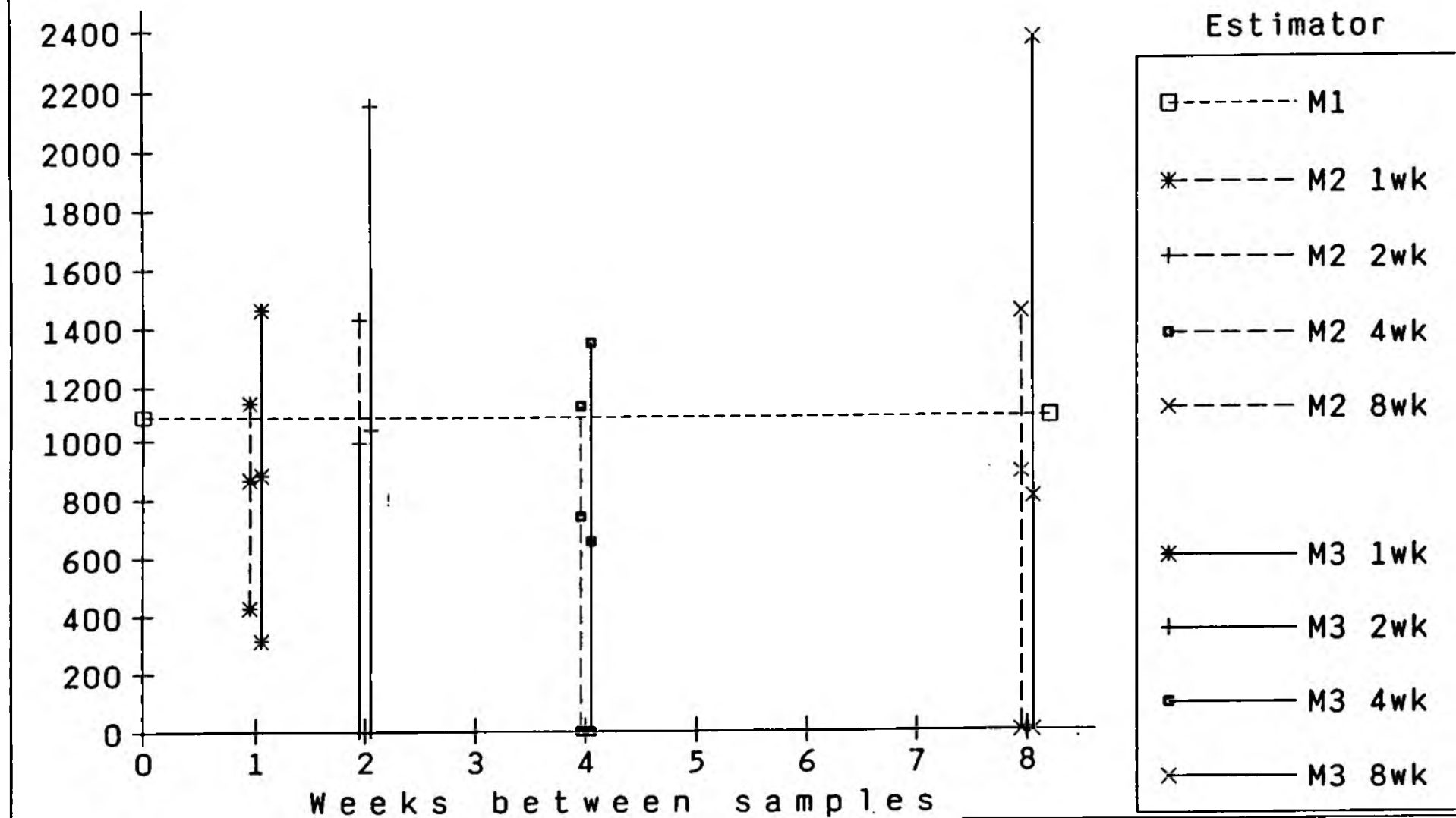


Fig.9: Load Estimates (Tonnes/Week) with 95% confidence limits
TP

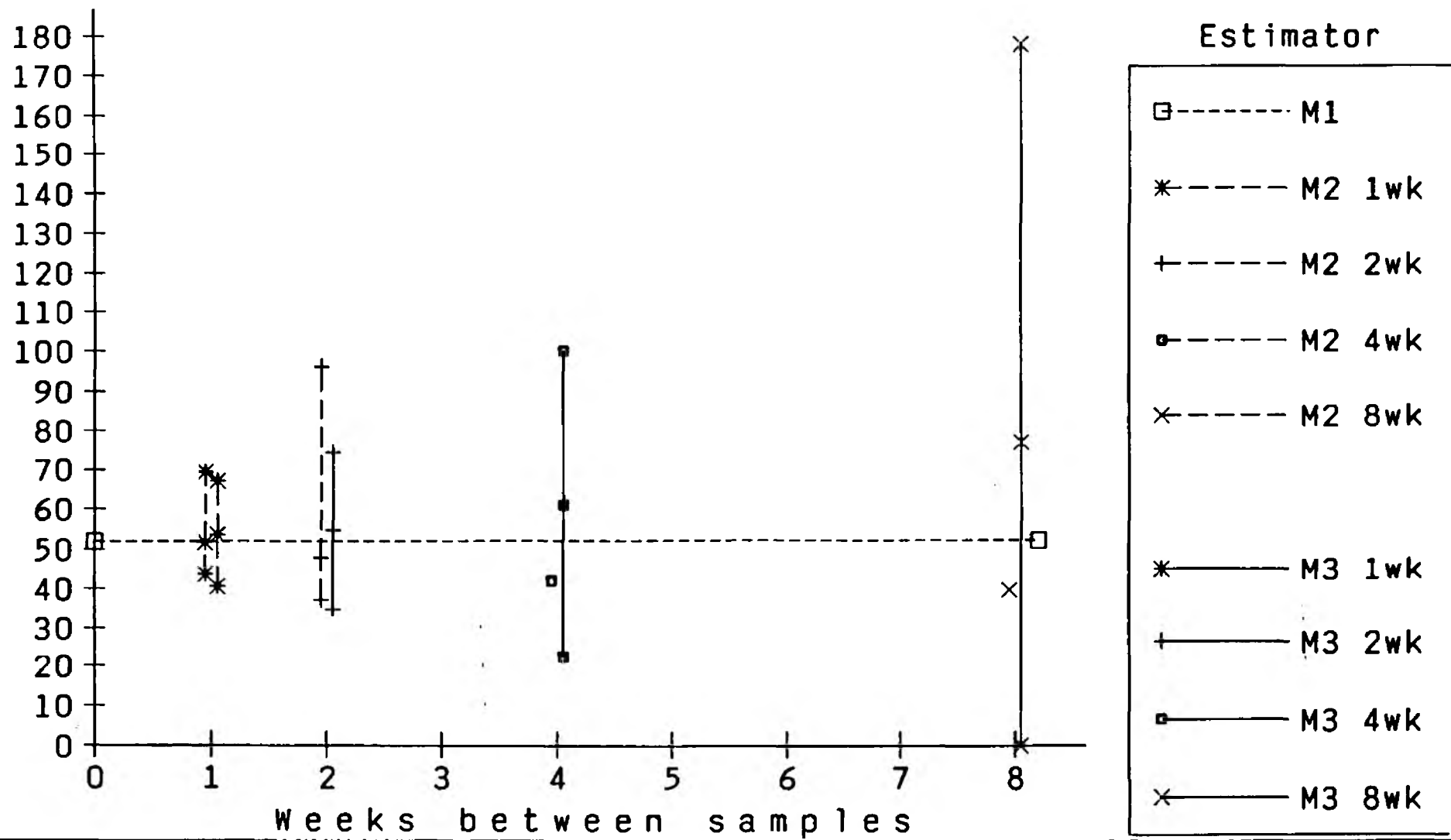


Fig.10: Load Estimates (Tonnes/Week) with 95% confidence limits
SRP

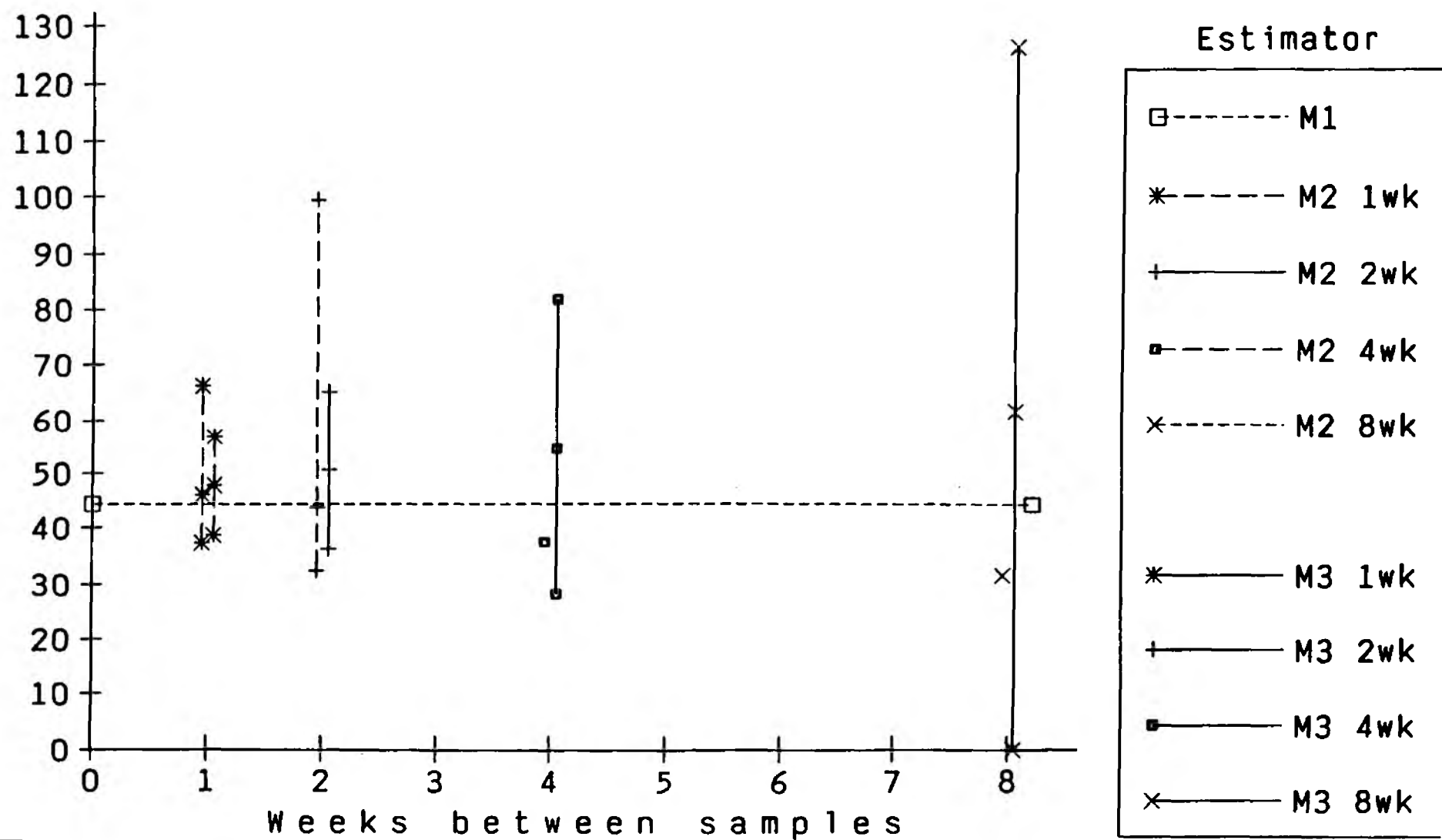


Fig.11: Load Estimates (Tonnes/Week) with 95% confidence limits
N03

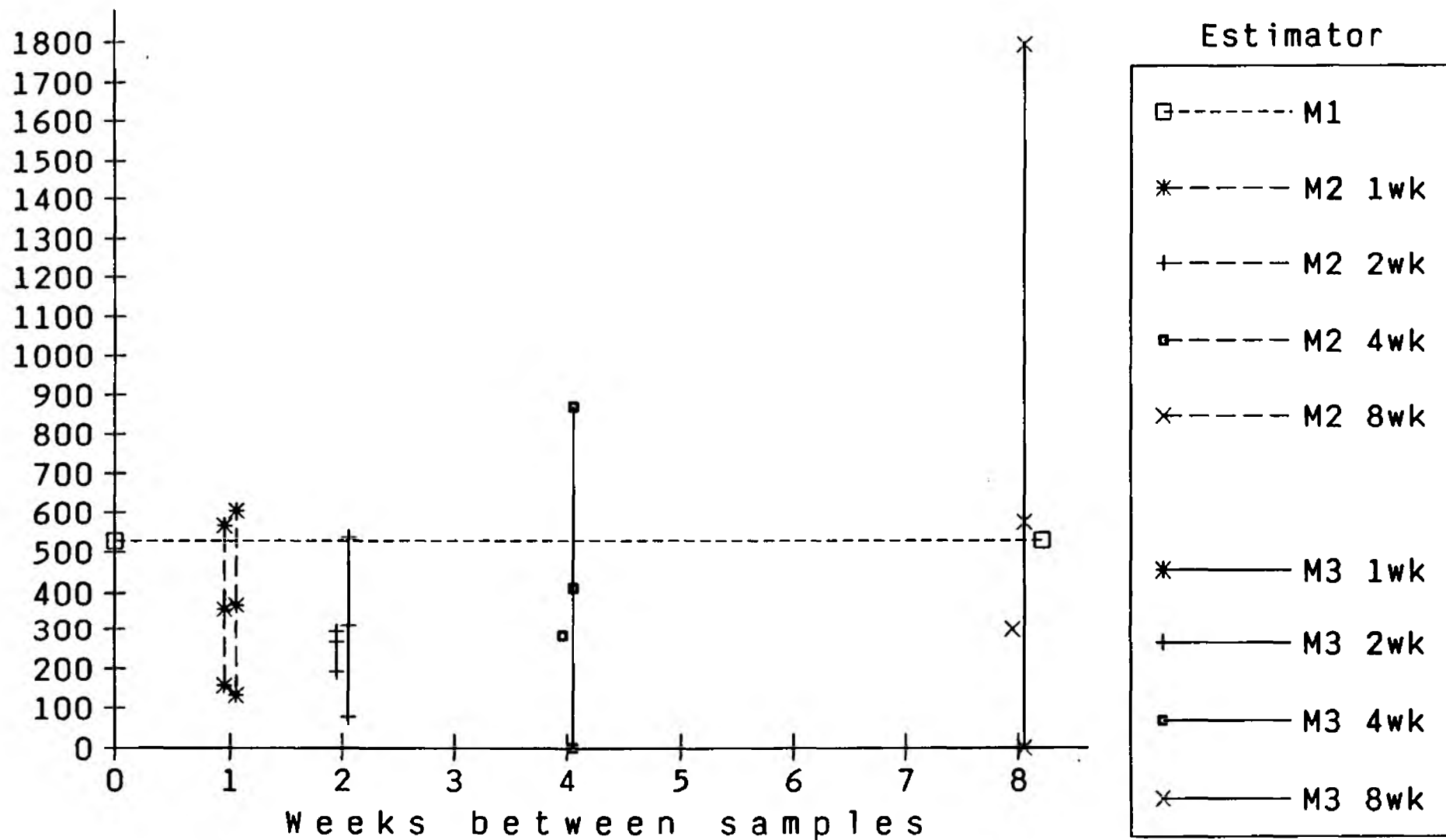


Figure 12. The relationship between grab sample concentration and instantaneous flow rate for Pb, Ni and Zn

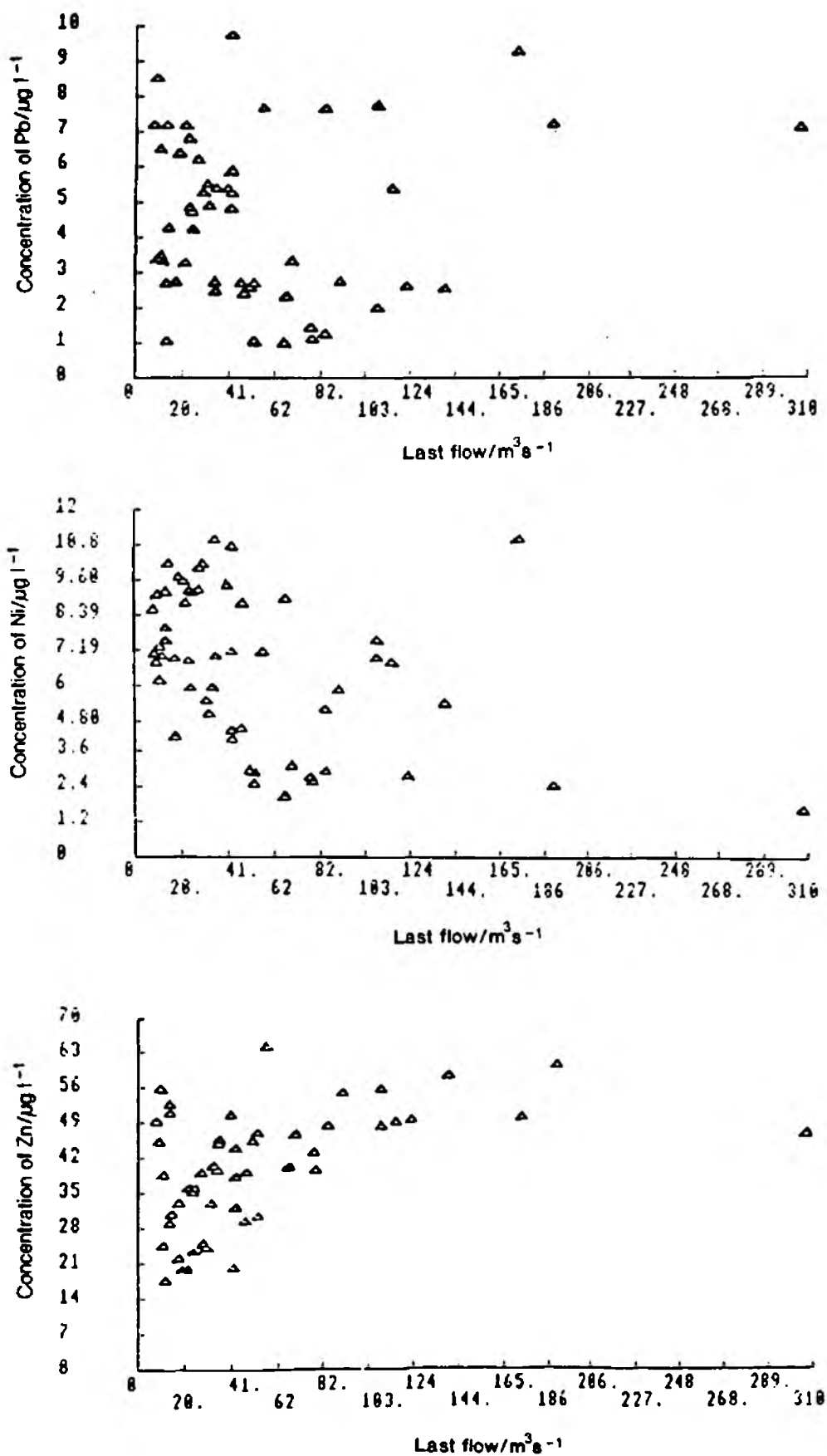


Figure 13. The relationship between grab sample concentration and instantaneous flow rate for Cd, Cr and Cu

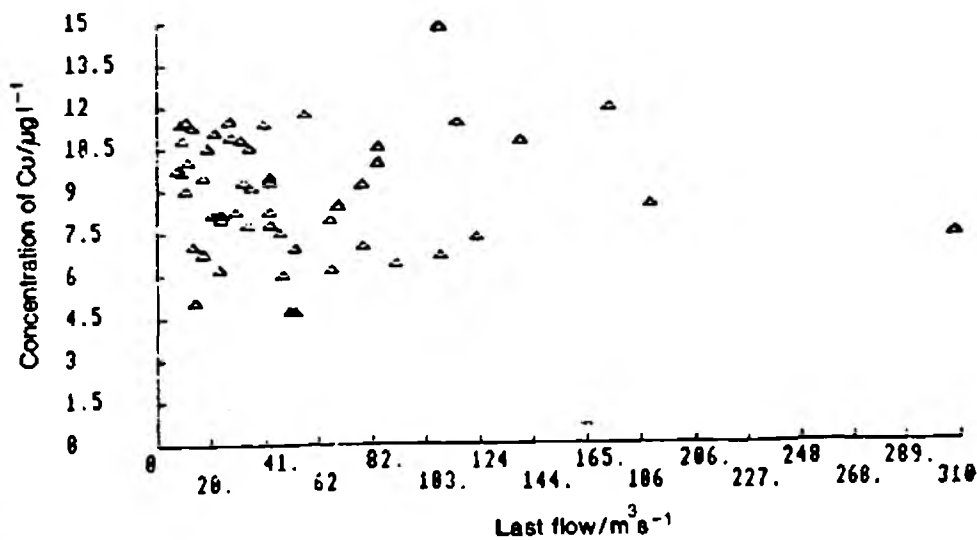
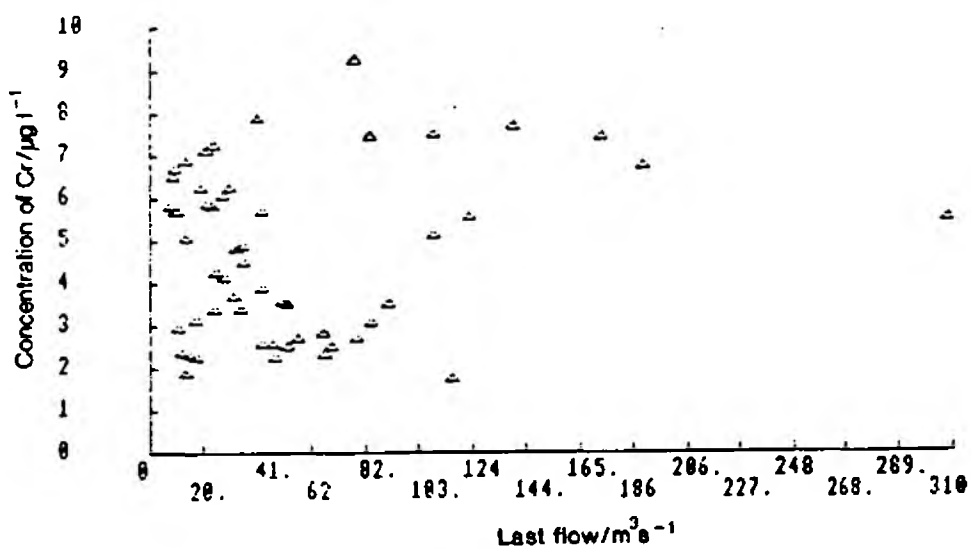
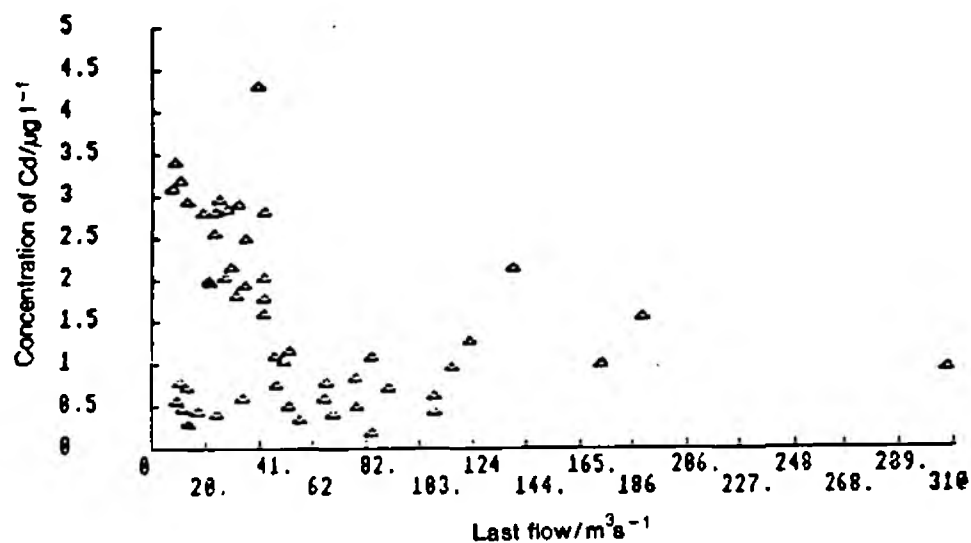


Figure 14. The relationship between grab sample concentration and instantaneous flow rate for TP, SRP and N/NO₃-

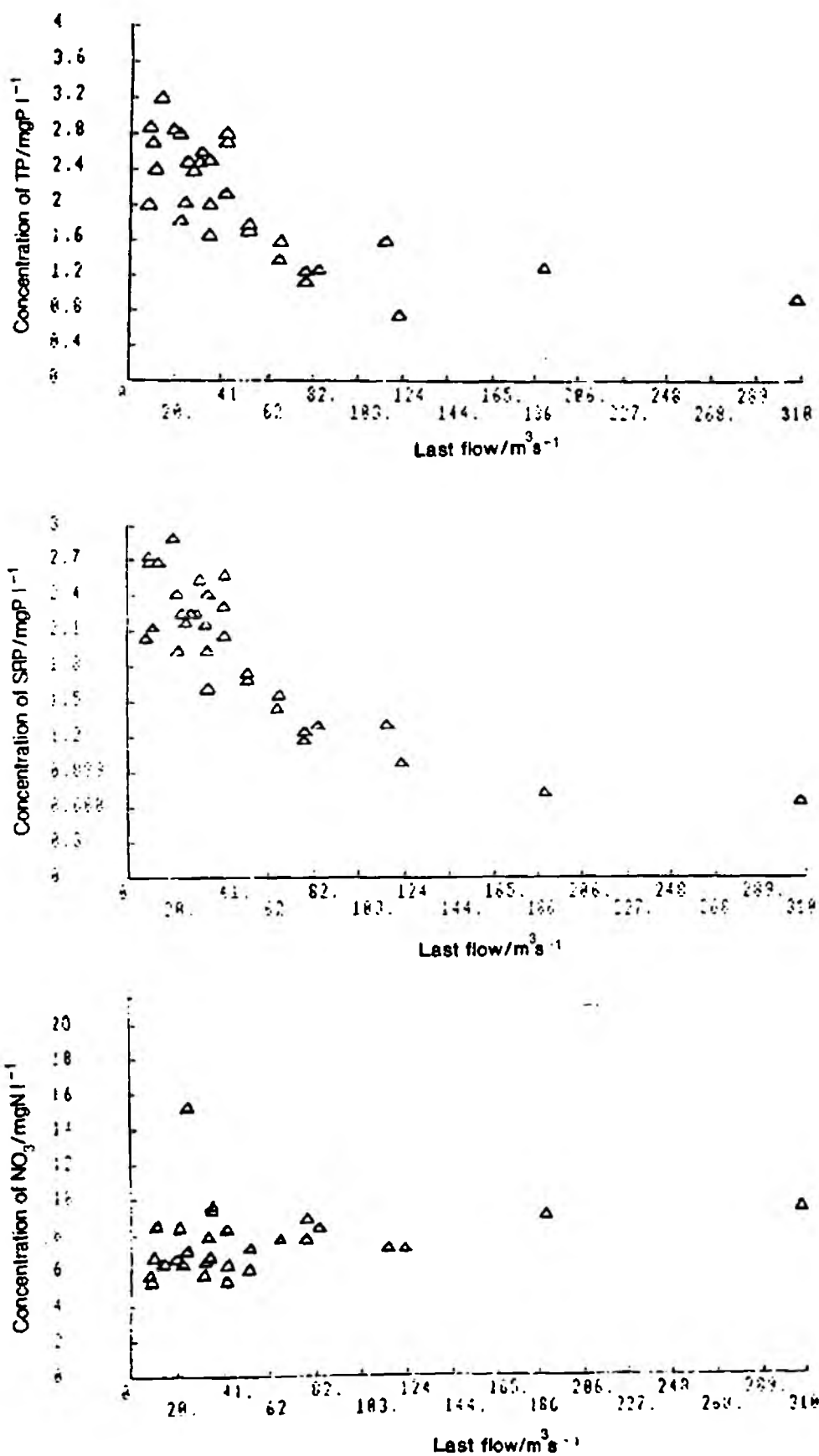


Figure 15. The relationship between grab sample concentration and instantaneous flow rate for Suspended Solids

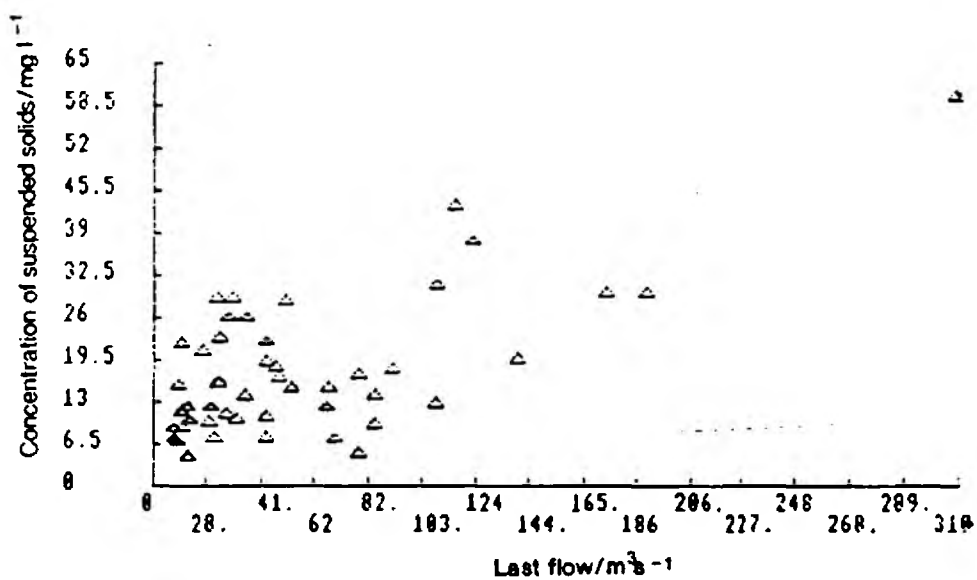


Figure 16. The relationship between composite sample concentration and average flow rate for Cd, Cr and Cu

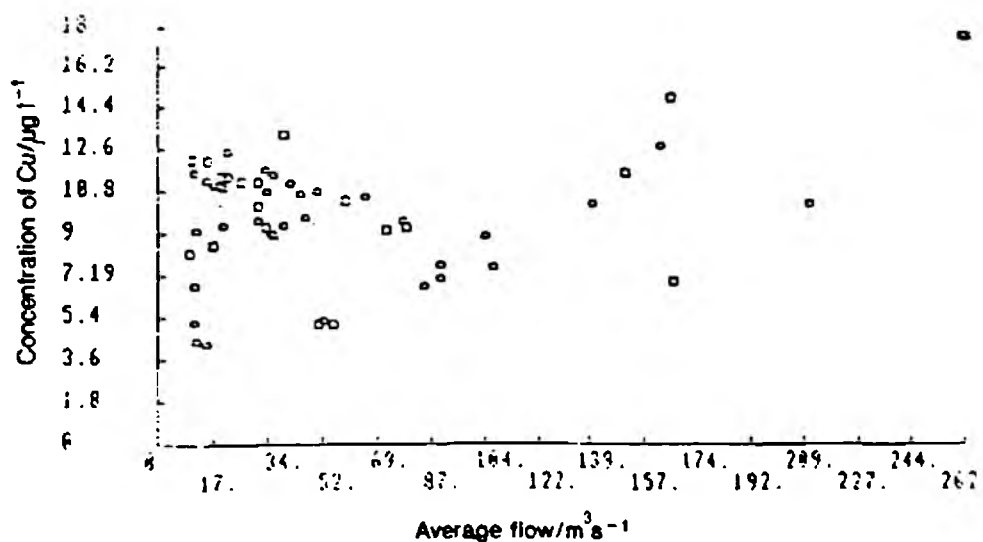
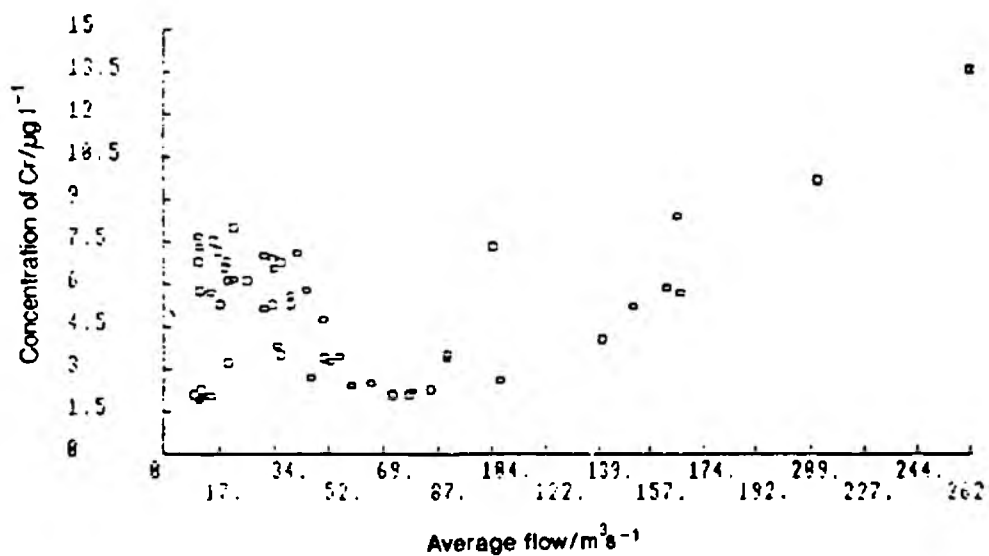
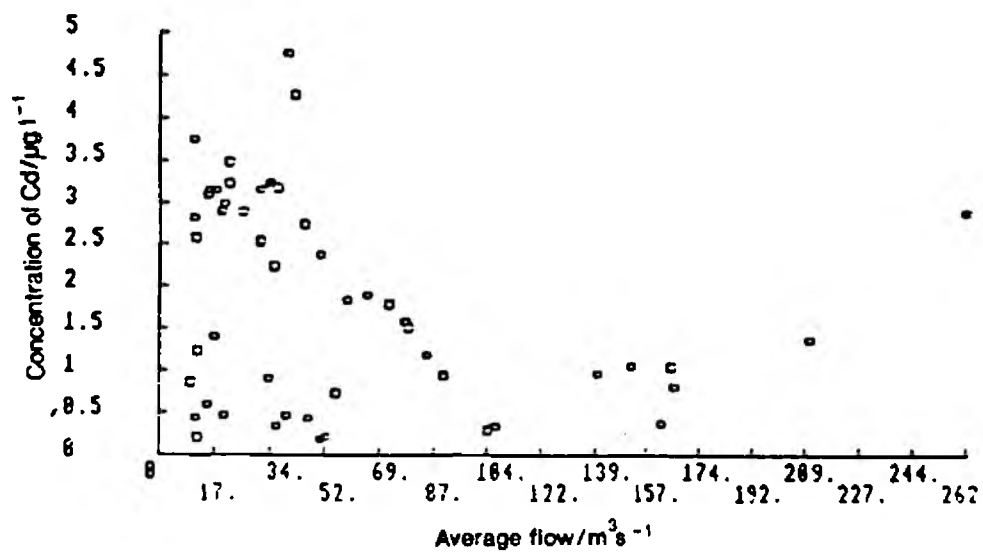


Figure 17. The relationship between composite sample concentrations and average flow rate for Pb, Ni and Zn

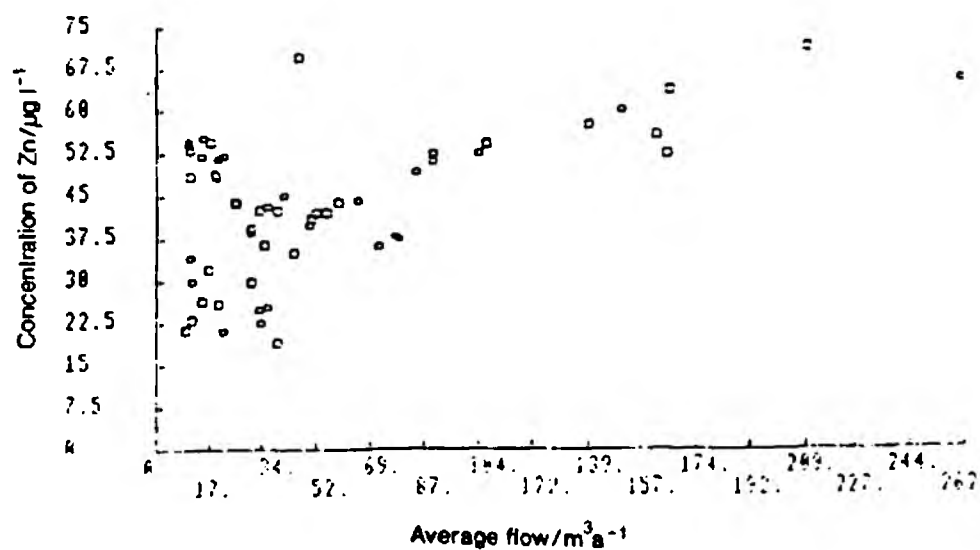
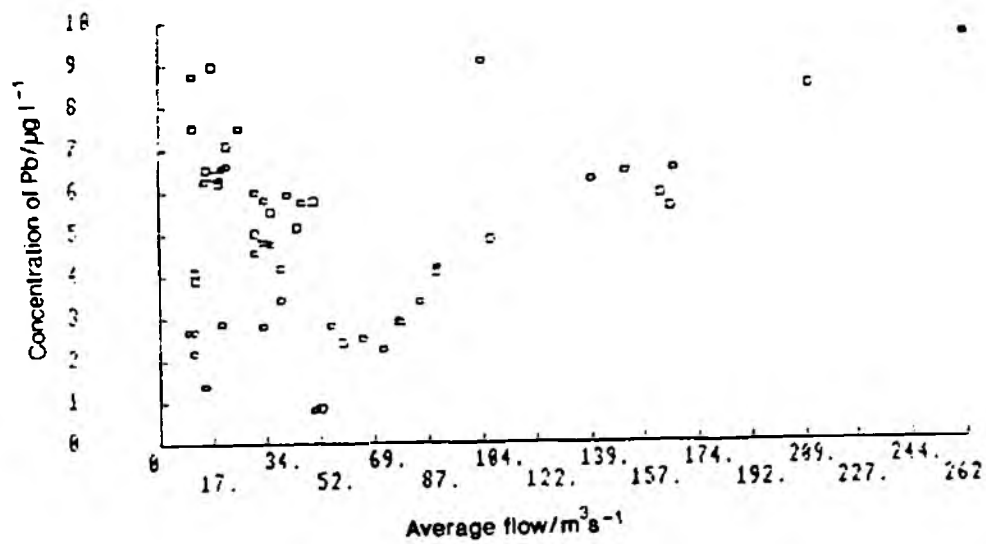
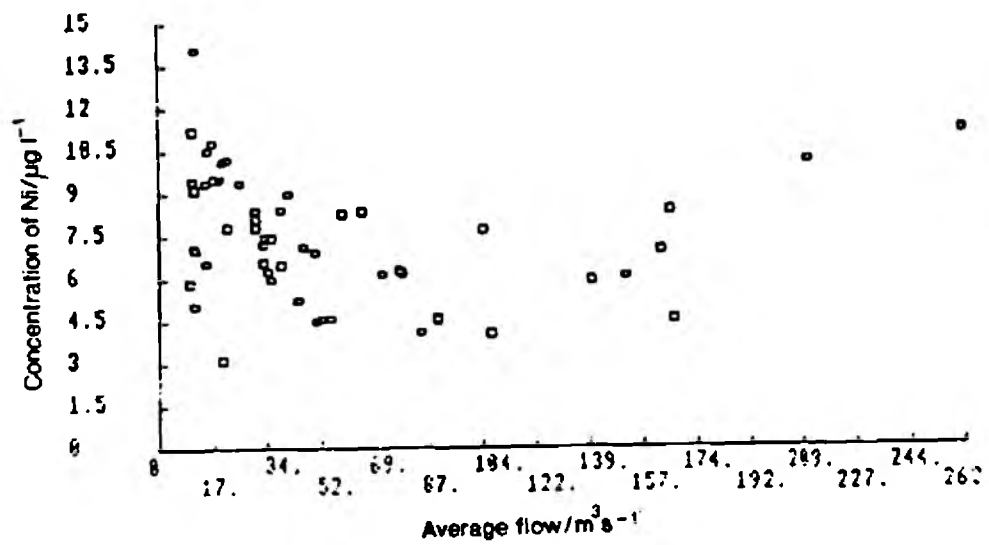


Figure 18. The relationship between composite sample concentration and average flow for TP, SRP and N/NO₃-

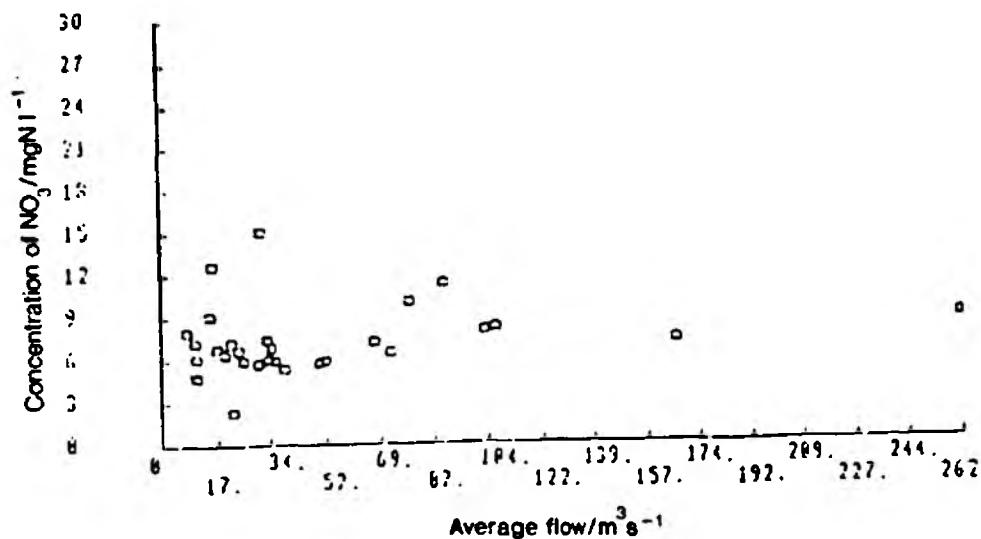
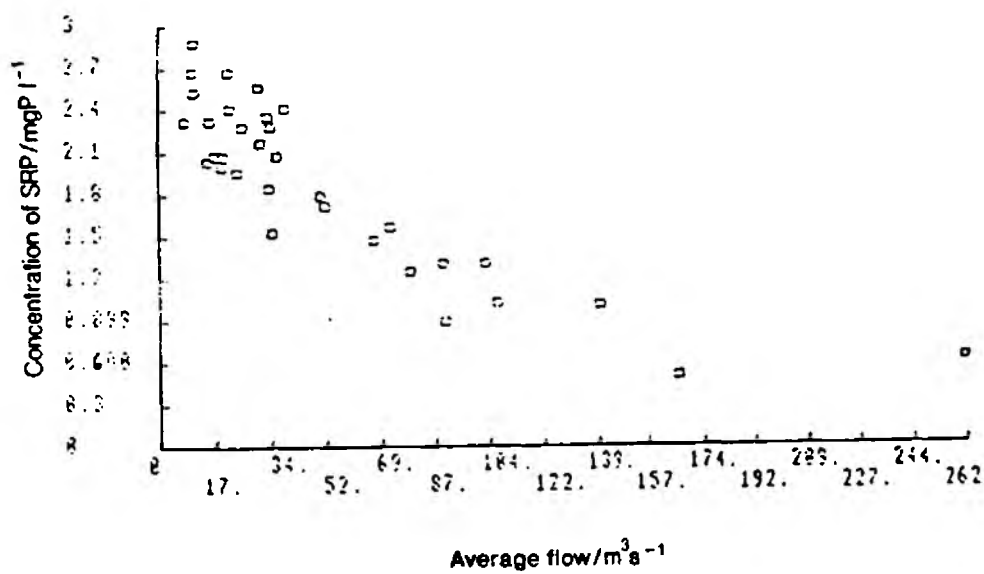
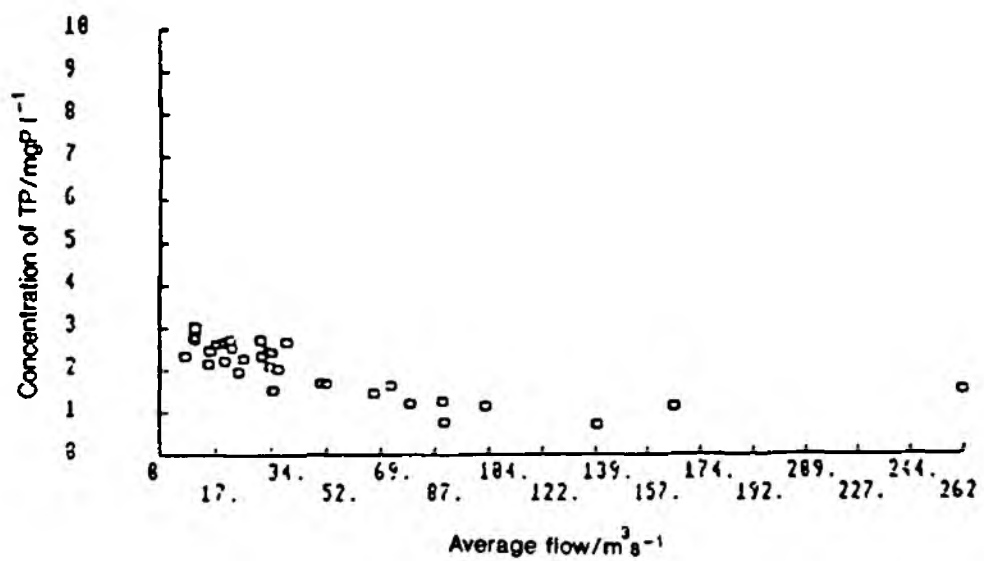


Figure 22. Relationship between concentrations of Cu and suspended solids in grab samples

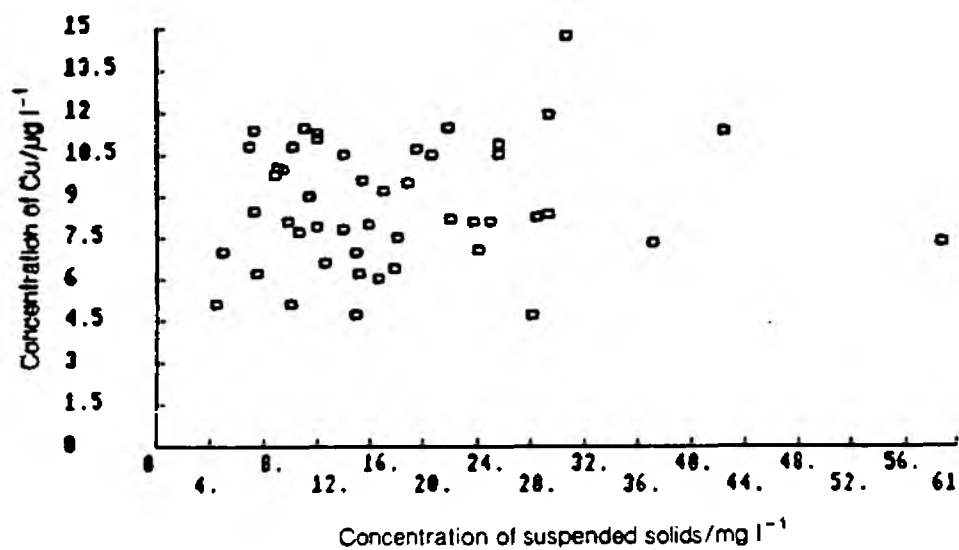


Figure 23. Relationship between concentrations of Ni and suspended solids in grab samples

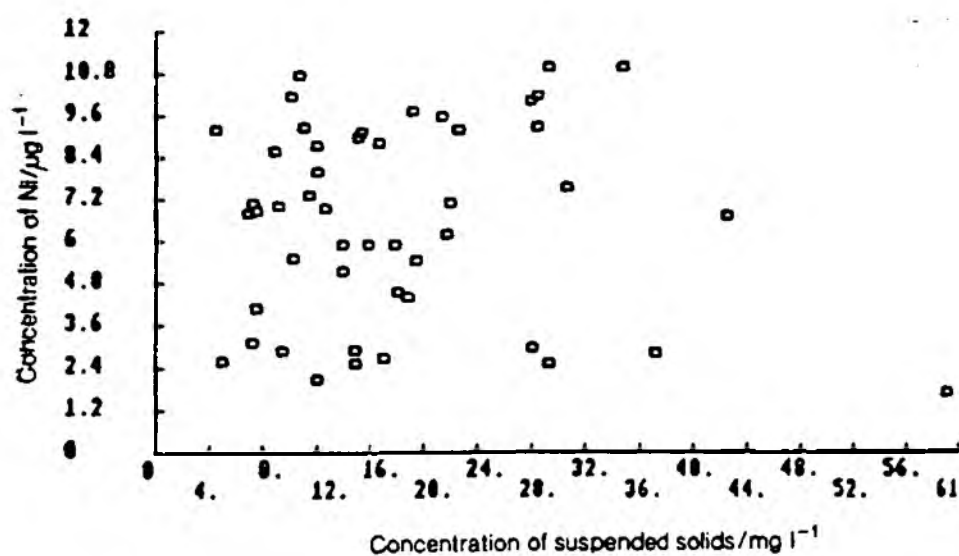


Figure 24. Relationship between concentrations of Pb and suspended solids in grab samples

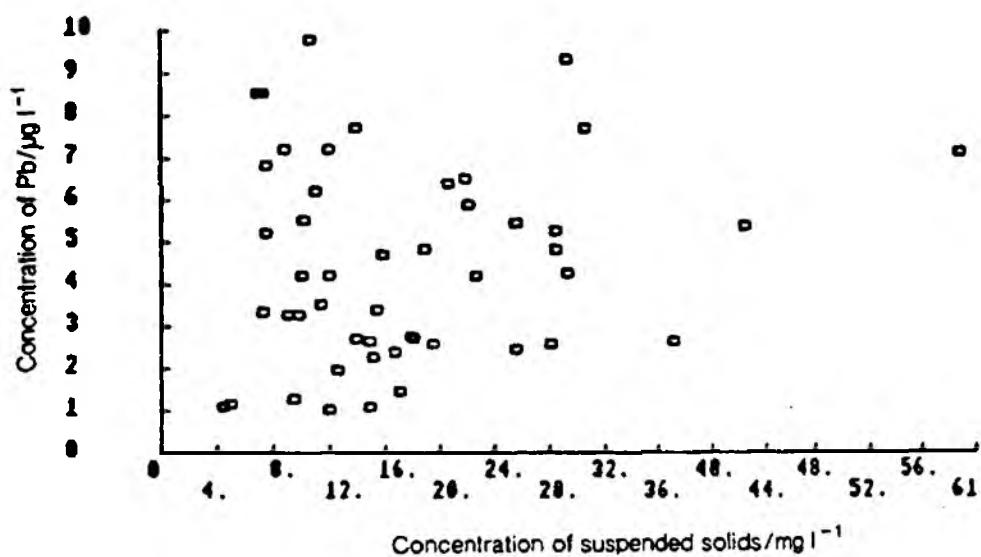


Figure 25. Relationship between concentrations of Zn and suspended solids in grab samples

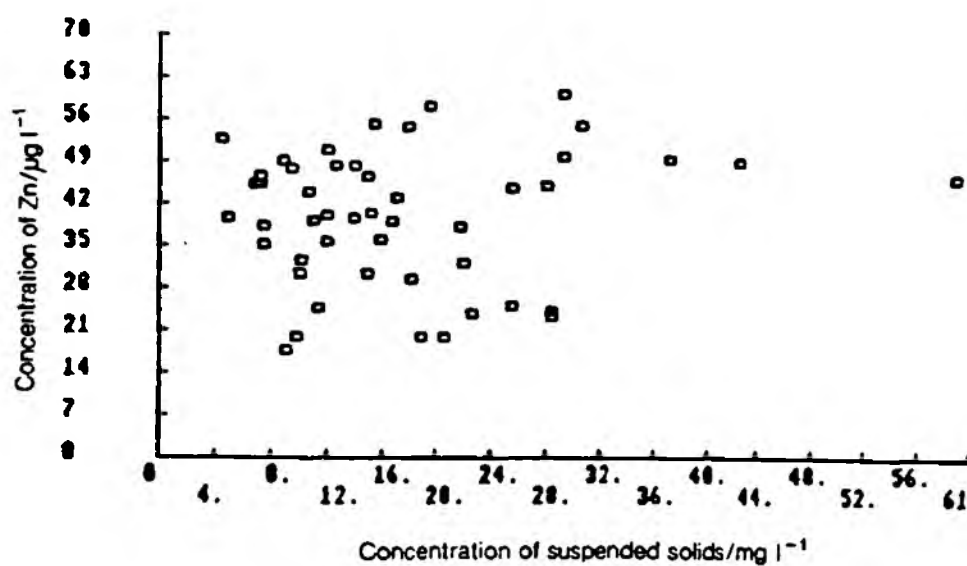


Figure 19. The relationship between composite sample concentration and average flow for Suspended Solids

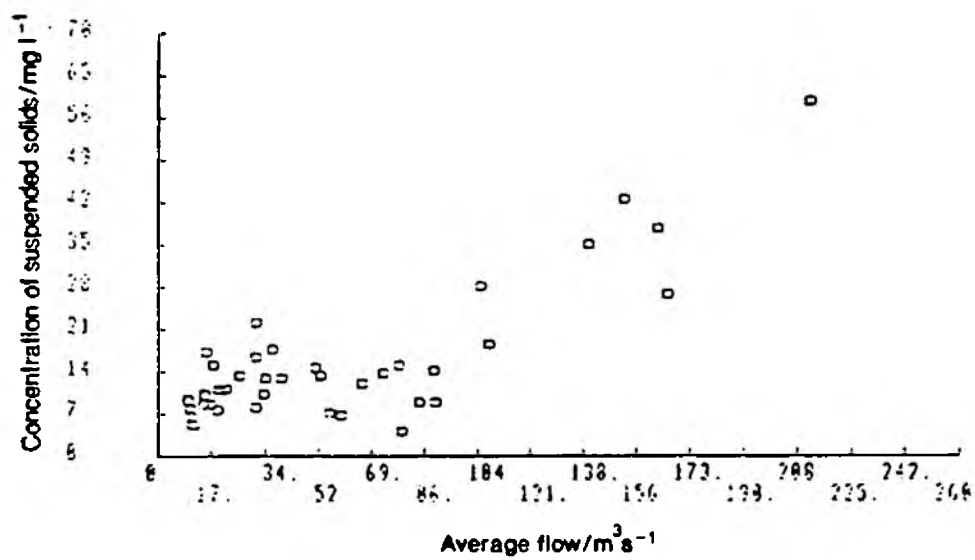


Figure 20. Relationship between concentrations of Cd and suspended solids in grab samples

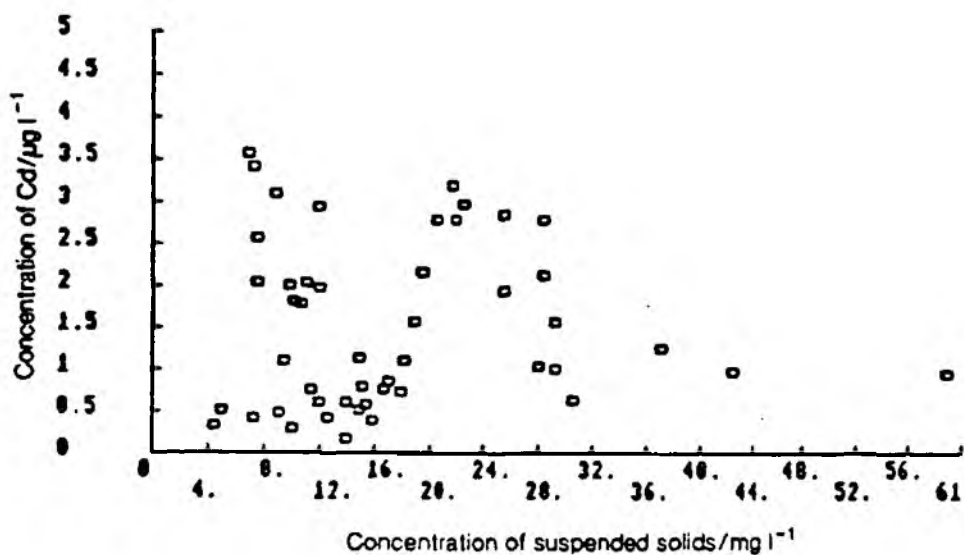


Figure 26. Relationship between concentrations of TP and suspended solids in grab samples

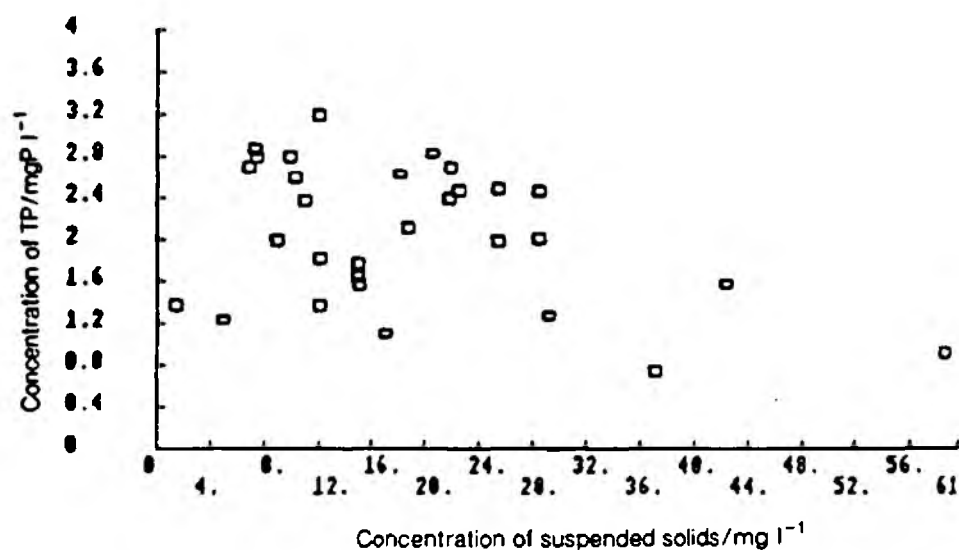


Figure 27. Relationship between concentrations of SRP and suspended solids in grab samples

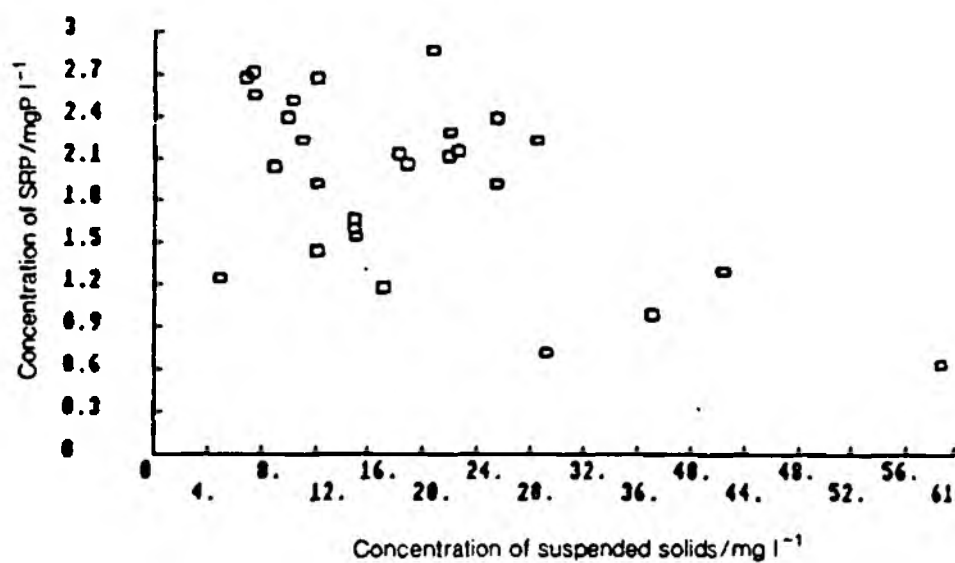
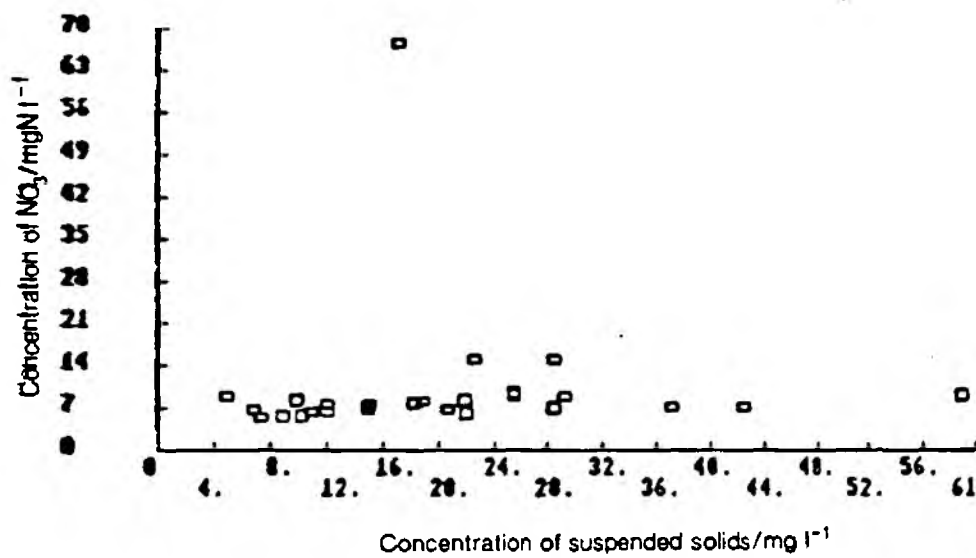


Figure 28. Relationship between concentrations of NO₃ and suspended solids in grab samples



APPENDIX A

**TRACE ELEMENT AND SUSPENDED SOLIDS CONCENTRATIONS IN COMPOSITE
AND GRAB SAMPLES AND FLOWS DURING JUNE 1987 TO DECEMBER 1988**

Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Concentration	
				Ni $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$
11.6.87	C	5.75	0.44	7.13	9.70
	G	7.71	0.34	7.13	11.70
18.6.87	C	5.93	4.26	9.00	11.14
	G	5.41	4.32	9.36	11.34
25.6.87	C	5.77	2.38	6.94	10.78
	G	5.41	2.51	7.02	9.11
2.7.87	C	5.17	2.74	5.26	10.68
	G	4.86	2.90	5.05	9.26
9.7.87	C	2.88	0.47	3.12	9.33
	G	2.77	0.45	4.25	6.77
16.7.87	C	2.69	0.44	5.05	6.73
	G	2.73	0.43	6.90	9.49
23.7.87	C	4.75	0.35	6.02	8.97
	G	4.72	0.40	5.92	7.97
30.7.87	C	8.98	1.40	10.78	8.47
	G	9.77	1.79	10.77	7.77
6.8.87	C	3.43	0.47	8.44	9.34
	G	3.42	0.58	9.13	9.65
13.8.87	C	2.68	0.86	5.84	8.18
	G	3.52	0.78	7.33	9.03
20.8.87	C	4.08	1.24	7.04	9.10
	G	3.31	0.49	7.00	10.08

Cr $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	SS mg l^{-1}	Flow average instantaneous $\text{m}^3 \text{s}^{-1}$
2.70	69.5	NM	46.7
2.70	64.0		64.0
7.12	44.9	NM	42.0
7.91	50.6		41.0
4.80	39.8	NM	50.8
4.50	45.8		36.0
5.82	34.9	NM	45.0
4.80	40.5		33.0
3.24	26.1	NM	20.4
3.15	21.8		18.0
1.89	34.2	NM	11.3
2.26	32.9		18.0
3.15	43.1	17.6	36.7
3.41	36.2	16.2	25.0
7.15	32.2	8.4	17.2
5.73	43.8	10.8	43.0
5.31	42.5	12.8	39.7
6.70	55.5	15.6	10.0
2.10	21.4	9.4	10.0
2.93	24.5	11.6	11.0
2.31	23.2	5.0	12.1
2.42	17.7	9.2	12.0

Continued

	Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$
A3	17.9.87	C	1.39	0.59
		G	2.72	0.73
	24.9.87	C	3.91	0.20
		G	4.24	0.29
	1.10.87	C	2.19	0.44
		G	1.08	0.32
	20.10.87	C	5.58	1.04
		G	7.74	0.63
	13.11.87	C	9.06	0.29
		G	7.71	0.18
	20.11.87	C	8.48	1.37
		G	9.34	1.01
	27.11.87	C	5.91	0.38
		G	1.99	0.43
	4.12.87	C	3.37	1.19
		G	3.33	0.41
	11.12.87	C	2.42	1.85
		G	2.38	0.76
	18.12.87	C	2.81	0.73
		G	2.77	0.73

Concentration					Flow average
Ni	Cu	Cr	Zn	SS	instantaneous
$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	mg l^{-1}	$\text{m}^3 \text{ s}^{-1}$
6.54	4.25	2.08	26.5	8.5	15.2
7.55	7.08	1.91	29.1	24.5	14.0
14.08	4.41	1.98	29.9	6.5	11.8
10.15	5.13	2.33	30.5	10.2	15.0
7.06	5.17	5.77	48.4	5.6	11.2
9.17	5.08	5.10	52.7	4.6	14.0
8.41	14.81	8.44	52.3	26.8	165.9
7.51	14.76	7.51	55.4	31.2	109.0
7.75	8.87	7.36	52.4	28.0	105.0
5.17	10.56	7.43	48.2	14.2	85.0
10.13	10.25	9.71	71.1	59.0	211.5
10.98	11.93	7.48	50.2	29.8	174.0
7.00	12.72	5.90	55.5	37.8	163.0
6.91	6.64	5.12	48.2	12.8	109.0
4.12	6.77	2.32	49.3	8.9	85.2
3.10	8.48	2.50	46.7	7.4	70.0
8.32	10.43	2.46	43.8	6.6	59.5
8.80	6.05	2.28	39.2	17.0	48.0
4.58	5.14	3.48	42.0	7.3	55.7
5.87	6.44	3.53	54.7	18.2	92.0

Continued

	Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Concentration	
					Ni $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$
A4	5.2.88	C	6.50	0.81	4.55	6.92
		G	7.13	0.94	1.70	7.36
	12.2.88	C	9.62	2.88	11.20	17.69
		G	4.28	1.58	2.52	8.43
	19.2.88	C	6.44	1.06	6.19	11.55
		G	2.57	2.17	5.45	10.75
	N 4.3.88	C	4.08	0.93	4.55	7.64
		G	1.26	1.10	2.91	9.95
	10.3.88	C	2.87	1.51	6.24	9.27
		G	1.17	0.51	2.58	7.02
	18.3.88	C	4.2	0.95	4.62	7.10
		G	1.48	0.85	2.69	9.25
	25.3.88	C	6.26	0.97	5.94	10.25
		G	2.67	1.28	2.83	7.38
	31.3.88	C	4.83	0.35	4.08	7.55
		G	5.42	0.98	6.74	11.39
	8.4.88	C	2.90	1.60	6.35	9.56
		G	1.00	0.60	2.08	7.95
	15.4.88	C	2.50	1.90	8.39	10.60
		G	2.30	0.80	8.95	6.20

Cr $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	SS mg l^{-1}	Flow average instantaneous $\text{m}^3 \text{s}^{-1}$
5.70	63.5	76.0	166.9
5.49	46.7	60.0	308.0
13.63	65.2	48.6	261.8
6.77	60.5	29.8	190.0
5.26	60.1	42.6	151.8
7.69	58.3	19.8	140.0
3.36	52.5	8.8	90.3
3.07	48.1	9.6	85.0
2.25	37.5	4.2	79.2
2.73	39.5	5.0	79.0
3.50	51.1	14.4	90.0
3.25	42.9	17.4	78.8
4.10	57.5	35.4	140.3
5.55	49.5	37.8	123.0
2.64	54.1	18.8	107.6
1.74	49.2	43.2	116.0
2.12	38.0	15.2	78.0
2.84	40.1	12.2	67.0
2.55	44.1	12.2	66.0
2.35	40.5	15.4	67.6

Continued

		Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Concentration	
Date of collection					Ni $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$
22.4.88		C	2.24	1.80	6.20	9.15
		G	1.10	0.50	2.50	7.00
N 6.5.88		C	0.80	0.19	4.50	5.10
		G	2.60	1.05	2.98	4.69
13.5.88		C	0.85	0.22	4.58	5.28
		G	2.68	1.15	2.85	4.70
26.5.88		C	2.80	0.91	6.59	9.30
		G	2.69	0.60	5.92	7.80
N 10.6.88		C	5.02	2.51	7.82	9.55
		G	2.70	1.10	4.52	7.50
17.6.88		C	6.25	3.10	9.38	11.25
		G	4.84	1.59	4.41	9.52
24.6.88		C	6.41	3.15	9.52	11.05
		G	5.92	2.81	7.12	8.24
1.7.88		C	6.61	3.23	10.20	11.41
		G	5.54	1.82	5.50	10.80
8.7.88		C	7.50	2.89	9.39	11.21
		G	4.20	1.99	8.77	11.10
15.7.88		C	6.55	3.00	10.12	10.95
		G	6.21	2.05	9.24	11.50

Cr $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	SS mg l^{-1}	Flow average instantaneous $\text{m}^3 \text{s}^{-1}$
2.10	36.1	13.8	73.0
2.50	30.4	15.2	53.0
3.40	41.0	14.8	51.0
3.60	45.2	28.6	51.0
3.30	41.9	13.4	52.4
3.49	46.8	15.2	53.0
5.30	42.5	10.2	34.4
3.40	39.5	14.2	35.0
5.15	38.5	22.1	31.7
2.55	29.4	18.5	47.0
5.71	52.1	10.2	15.2
2.59	20.1	19.2	43.0
5.28	54.5	15.2	17.6
3.91	32.1	22.4	43.0
6.20	52.1	11.2	22.2
3.70	32.8	10.4	32.0
6.15	43.9	13.4	26.0
5.92	35.8	12.2	22.5
6.15	51.5	10.7	20.3
6.05	39.2	11.2	28.0

Continued

	Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$
	26.8.88	C	8.75	3.75
		G	8.54	3.58
	2.9.88	C	6.54	3.15
		G	6.51	3.20
	9.9.88	C	6.32	2.91
		G	7.20	3.10
	16.9.88	C	7.54	2.82
		G	8.50	3.42
	23.9.88	C	7.50	2.58
		G	7.21	2.94
	29.9.88	C	4.55	2.54
		G	5.25	2.05
N	22.10.88	C	6.21	2.89
		G	6.85	2.58
	28.10.88	C	6.01	3.15
		G	5.28	2.15
	4.11.88	C	5.82	3.25
		G	4.22	2.98
	11.11.88	C	5.54	3.17
		G	4.85	2.81

Concentration					Flow average
Ni	Cu	Cr	Zn	SS	instantaneous
$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	mg l^{-1}	$\text{m}^3 \text{ s}^{-1}$
11.20	12.20	6.81	54.1	7.6	10.7
6.77	10.80	5.69	45.2	7.0	10.0
10.50	12.10	7.55	55.2	17.2	15.7
6.20	11.50	5.68	38.4	22.2	11.0
9.55	11.40	6.81	48.4	11.0	19.6
8.58	9.80	5.82	49.1	9.0	8.0
9.45	12.10	7.68	54.8	7.8	11.0
7.10	11.40	6.51	45.2	7.4	9.0
9.15	11.59	7.29	53.1	8.2	11.2
8.00	11.29	6.91	50.9	12.2	14.0
8.10	10.20	5.15	39.1	8.2	31.3
4.12	9.35	3.92	38.2	7.6	43.0
9.45	11.00	6.59	49.1	7.8	19.4
6.85	6.21	5.81	35.2	7.6	24.0
8.42	11.20	7.02	29.8	16.3	31.5
10.15	8.28	6.25	24.2	29.0	30.2
7.51	10.80	6.58	22.5	23.1	34.8
9.15	8.15	4.29	23.8	23.0	25.4
7.45	11.50	6.82	25.2	27.0	36.9
9.28	8.15	7.28	23.4	29.0	24.2

Continued

Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Concentration		Cr $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	SS mg l^{-1}	Flow average instantaneous $\text{m}^3 \text{s}^{-1}$
				Ni $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$				
18.11.88	C	4.82	3.22	7.20	11.70	6.95	24.8	27.9	33.9
	G	3.29	2.02	9.54	8.15	7.12	19.9	10.0	21.8
24.11.88	C	7.10	3.48	7.82	12.50	8.02	21.1	18.3	21.9
	G	6.42	2.81	9.72	10.50	6.25	19.7	21.0	19.6
9.12.88	C	4.18	4.75	6.52	13.20	5.62	19.0	46.9	39.9
	G	2.48	1.94	10.99	10.50	4.92	44.7	26.0	35.4
19.12.88	C	4.82	2.23	6.27	9.00	3.86	36.2	41.5	35.6
	G	5.45	2.85	9.99	10.92	4.15	25.1	26.0	28.5

N = not used in load calculations

Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$
11.6.87	C	5.75	0.44
	G	7.71	0.34
18.6.87	C	5.93	4.26
	G	5.41	4.32
25.6.87	C	5.77	2.38
	G	5.41	2.51
2.7.87	C	5.17	2.74
	G	4.86	2.90
9.7.87	C	2.88	0.47
	G	2.77	0.45
16.7.87	C	2.69	0.44
	G	2.73	0.43
23.7.87	C	4.75	0.35
	G	4.72	0.40
30.7.87	C	8.98	1.40
	G	9.77	1.79
6.8.87	C	3.43	0.47
	G	3.42	0.58
13.8.87	C	2.68	0.86
	G	3.52	0.78
20.8.87	C	4.08	1.24
	G	3.31	0.49

Concentration					Flow average
Ni	Cu	Cr	Zn	SS	instantaneous
$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	mg l^{-1}	$\text{m}^3 \text{s}^{-1}$
7.13	9.70	2.70	69.5	NM	46.7
7.13	11.70	2.70	64.0		64.0
9.00	11.14	7.12	44.9	NM	42.0
9.36	11.34	7.91	50.6		41.0
6.94	10.78	4.80	39.8	NM	50.8
7.02	9.11	4.50	45.8		36.0
5.26	10.68	5.82	34.9	NM	45.0
5.05	9.26	4.80	40.5		33.0
3.12	9.33	3.24	26.1	NM	20.4
4.25	6.77	3.15	21.8		18.0
5.05	6.73	1.89	34.2	NM	11.3
6.90	9.49	2.26	32.9		18.0
6.02	8.97	3.15	43.1	17.6	36.7
5.92	7.97	3.41	36.2	16.2	25.0
10.78	8.47	7.15	32.2	8.4	17.2
10.77	7.77	5.73	43.8	10.8	43.0
8.44	9.34	5.31	42.5	12.8	39.7
9.13	9.65	6.70	55.5	15.6	10.0
5.84	8.18	2.10	21.4	9.4	10.0
7.33	9.03	2.93	24.5	11.6	11.0
7.04	9.10	2.31	23.2	5.0	12.1
7.00	10.08	2.42	17.7	9.2	12.0

Continued

	Date of collection	Type of sample	Pb ug l ⁻¹	Cd ug l ⁻¹	Concentration		Cr ug l ⁻¹	Zn ug l ⁻¹	SS mg l ⁻¹	Flow average instantaneous m ³ s ⁻¹
					Ni ug l ⁻¹	Cu ug l ⁻¹				
N	17.9.87	C	1.39	0.59	6.54	4.25	2.08	26.5	8.5	15.2
		G	2.72	0.73	7.55	7.08	1.91	29.1	24.5	14.0
	24.9.87	C	3.91	0.20	14.08	4.41	1.98	29.9	6.5	11.8
		G	4.24	0.29	10.15	5.13	2.33	30.5	10.2	15.0
	1.10.87	C	2.19	0.44	7.06	5.17	5.77	48.4	5.6	11.2
		G	1.08	0.32	9.17	5.08	5.10	52.7	4.6	14.0
N	20.10.87	C	5.58	1.04	8.41	14.81	8.44	52.3	26.8	165.9
		G	7.74	0.63	7.51	14.76	7.51	55.4	31.2	109.0
N	13.11.87	C	9.06	0.29	7.75	8.87	7.36	52.4	28.0	105.0
		G	7.71	0.18	5.17	10.56	7.43	48.2	14.2	85.0
	20.11.87	C	8.48	1.37	10.13	10.25	9.71	71.1	59.0	211.5
		G	9.34	1.01	10.98	11.93	7.48	50.2	29.8	174.0
	27.11.87	C	5.91	0.38	7.00	12.72	5.90	55.5	37.8	163.0
		G	1.99	0.43	6.91	6.64	5.12	48.2	12.8	109.0
	4.12.87	C	3.37	1.19	4.12	6.77	2.32	49.3	8.9	85.2
		G	3.33	0.41	3.10	8.48	2.50	46.7	7.4	70.0
	11.12.87	C	2.42	1.85	8.32	10.43	2.46	43.8	6.6	59.5
		G	2.38	0.76	8.80	6.05	2.28	39.2	17.0	48.0
	18.12.87	C	2.81	0.73	4.58	5.14	3.48	42.0	7.3	55.7
		G	2.77	0.73	5.87	6.44	3.53	54.7	18.2	92.0

Continued

A10

	Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$
	5.2.88	C	6.50	0.81
		G	7.13	0.94
	12.2.88	C	9.62	2.88
		G	4.28	1.58
	19.2.88	C	6.44	1.06
		G	2.57	2.17
N	4.3.88	C	4.08	0.93
		G	1.26	1.10
	10.3.88	C	2.87	1.51
		G	1.17	0.51
	18.3.88	C	4.2	0.95
		G	1.48	0.85
	25.3.88	C	6.26	0.97
		G	2.67	1.28
	31.3.88	C	4.83	0.35
		G	5.42	0.98
	8.4.88	C	2.90	1.60
		G	1.00	0.60
	15.4.88	C	2.50	1.90
		G	2.30	0.80

Concentration					Flow average
Ni	Cu	Cr	Zn	SS	instantaneous
$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	mg l^{-1}	$\text{m}^3 \text{s}^{-1}$
4.55	6.92	5.70	63.5	76.0	166.9
1.70	7.36	5.49	46.7	60.0	308.0
11.20	17.69	13.63	65.2	48.6	261.8
2.52	8.43	6.77	60.5	29.8	190.0
6.19	11.55	5.26	60.1	42.6	151.8
5.45	10.75	7.69	58.3	19.8	140.0
4.55	7.64	3.36	52.5	8.8	90.3
2.91	9.95	3.07	48.1	9.6	85.0
6.24	9.27	2.25	37.5	4.2	79.2
2.58	7.02	2.73	39.5	5.0	79.0
4.62	7.10	3.50	51.1	14.4	90.0
2.69	9.25	3.25	42.9	17.4	78.8
5.94	10.25	4.10	57.5	35.4	140.3
2.83	7.38	5.55	49.5	37.8	123.0
4.08	7.55	2.64	54.1	18.8	107.6
6.74	11.39	1.74	49.2	43.2	116.0
6.35	9.56	2.12	38.0	15.2	78.0
2.08	7.95	2.84	40.1	12.2	67.0
8.39	10.60	2.55	44.1	12.2	66.0
8.95	6.20	2.35	40.5	15.4	67.6

Continued

	Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Concentration		Cr $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	SS mg l^{-1}	Flow average instantaneous $\text{m}^3 \text{s}^{-1}$
					Ni $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$				
N	22.4.88	C	2.24	1.80	6.20	9.15	2.10	36.1	13.8	73.0
		G	1.10	0.50	2.50	7.00	2.50	30.4	15.2	53.0
	6.5.88	C	0.80	0.19	4.50	5.10	3.40	41.0	14.8	51.0
		G	2.60	1.05	2.98	4.69	3.60	45.2	28.6	51.0
N	13.5.88	C	0.85	0.22	4.58	5.28	3.30	41.9	13.4	52.4
		G	2.68	1.15	2.85	4.70	3.49	46.8	15.2	53.0
	26.5.88	C	2.80	0.91	6.59	9.30	5.30	42.5	10.2	34.4
		G	2.69	0.60	5.92	7.80	3.40	39.5	14.2	35.0
	10.6.88	C	5.02	2.51	7.82	9.55	5.15	38.5	22.1	31.7
		G	2.70	1.10	4.52	7.50	2.55	29.4	18.5	47.0
	17.6.88	C	6.25	3.10	9.38	11.25	5.71	52.1	10.2	15.2
		G	4.84	1.59	4.41	9.52	2.59	20.1	19.2	43.0
	24.6.88	C	6.41	3.15	9.52	11.05	5.28	54.5	15.2	17.6
		G	5.92	2.81	7.12	8.24	3.91	32.1	22.4	43.0
	1.7.88	C	6.61	3.23	10.20	11.41	6.20	52.1	11.2	22.2
		G	5.54	1.82	5.50	10.80	3.70	32.8	10.4	32.0
	8.7.88	C	7.50	2.89	9.39	11.21	6.15	43.9	13.4	26.0
		G	4.20	1.99	8.77	11.10	5.92	35.8	12.2	22.5
	15.7.88	C	6.55	3.00	10.12	10.95	6.15	51.5	10.7	20.3
		G	6.21	2.05	9.24	11.50	6.05	39.2	11.2	28.0

Continued

	Date of collection	Type of sample	Pb $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Concentration	
					Ni $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$
A12	26.8.88	C	8.75	3.75	11.20	12.20
		G	8.54	3.58	6.77	10.80
	2.9.88	C	6.54	3.15	10.50	12.10
		G	6.51	3.20	6.20	11.50
	9.9.88	C	6.32	2.91	9.55	11.40
		G	7.20	3.10	8.58	9.80
	16.9.88	C	7.54	2.82	9.45	12.10
		G	8.50	3.42	7.10	11.40
	23.9.88	C	7.50	2.58	9.15	11.59
		G	7.21	2.94	8.00	11.29
	29.9.88	C	4.55	2.54	8.10	10.20
		G	5.25	2.05	4.12	9.35
	N 22.10.88	C	6.21	2.89	9.45	11.00
		G	6.85	2.58	6.85	6.21
	28.10.88	C	6.01	3.15	8.42	11.20
		G	5.28	2.15	10.15	8.28
	4.11.88	C	5.82	3.25	7.51	10.80
		G	4.22	2.98	9.15	8.15
	11.11.88	C	5.54	3.17	7.45	11.50
		G	4.85	2.81	9.28	8.15

Cr $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	SS mg l^{-1}	Flow average instantaneous $\text{m}^3 \text{s}^{-1}$
6.81	54.1	7.6	10.7
5.69	45.2	7.0	10.0
7.55	55.2	17.2	15.7
5.68	38.4	22.2	11.0
6.81	48.4	11.0	19.6
5.82	49.1	9.0	8.0
7.68	54.8	7.8	11.0
6.51	45.2	7.4	9.0
7.29	53.1	8.2	11.2
6.91	50.9	12.2	14.0
5.15	39.1	8.2	31.3
3.92	38.2	7.6	43.0
6.59	49.1	7.8	19.4
5.81	35.2	7.6	24.0
7.02	29.8	16.3	31.5
6.25	24.2	29.0	30.2
6.58	22.5	23.1	34.8
4.29	23.8	23.0	25.4
6.82	25.2	27.0	36.9
7.28	23.4	29.0	24.2

Continued

Date of collection	Type of sample	Concentration							Flow average instantaneous m ³ s ⁻¹
		Pb μg l ⁻¹	Cd μg l ⁻¹	Ni μg l ⁻¹	Cu μg l ⁻¹	Cr μg l ⁻¹	Zn μg l ⁻¹	SS mg l ⁻¹	
18.11.88	C	4.82	3.22	7.20	11.70	6.95	24.8	27.9	33.9
	G	3.29	2.02	9.54	8.15	7.12	19.9	10.0	21.8
24.11.88	C	7.10	3.48	7.82	12.50	8.02	21.1	18.3	21.9
	G	6.42	2.81	9.72	10.50	6.25	19.7	21.0	19.6
9.12.88	C	4.18	4.75	6.52	13.20	5.62	19.0	46.9	39.9
	G	2.48	1.94	10.99	10.50	4.92	44.7	26.0	35.4
19.12.88	C	4.82	2.23	6.27	9.00	3.86	36.2	41.5	35.6
	G	5.45	2.85	9.99	10.92	4.15	25.1	26.0	28.5

N = not used in load calculations

**APPENDIX B - TOTAL PHOSPHORUS, SOLUBLE REACTIVE PHOSPHATE
AND NITRATE CONCENTRATIONS IN COMPOSITE GRAB SAMPLES DURING
FEBRUARY 1988 TO DECEMBER 1988**

	Data of collection	Type of sample	Concentration		NO ₃ mg N l ⁻¹	Flow average instantaneous m ³ s ⁻¹
			TP mg P l ⁻¹	SRP mg P l ⁻¹		
N	5.2.88	C	1.17	0.50	7.15	166.9
		G	0.92	0.65	9.25	308.0
	12.2.88	C	1.52	0.60	8.69	261.8
		G	1.29	0.72	8.98	190.0
	4.3.88	C	0.76	0.90	11.29	90.3
		G	1.26	1.30	8.35	85.0
	10.3.88	C	1.19	1.24	10.04	79.2
		G	1.24	1.25	8.86	79.0
	18.3.88	C	1.26	1.30	114.60	90.0
		G	1.11	1.18	67.70	78.8
	25.3.88	C	0.69	1.01	37.80	140.3
		G	0.75	0.99	7.23	123.0
	31.3.88	C	1.15	1.05	8.19	107.6
		G	1.59	1.30	7.18	116.0
	8.4.88	C	1.17	1.30	7.97	78.0
		G	1.37	1.44	7.63	67.0
	15.4.88	C	1.46	1.47	7.23	66.0
		G	1.58	1.55	7.63	67.6
	22.4.88	C	1.65	1.56	6.50	73.0
		G	1.78	1.67	7.23	53.0
	6.5.88	C	1.74	1.80	5.64	51.0
		G	1.74	1.88	6.35	51.0
	13.5.88	C	1.74	1.72	5.99	52.4
		G	1.70	1.73	5.99	53.0
	19.5.88	C	1.60	1.65	7.06	35.3
		G	1.65	1.60	6.70	41.0
	26.5.88	C	2.10	1.84	6.10	34.4
		G	2.64	2.14	7.85	35.0

Appendix B - Continued

	Data of collection	Type of sample	TP mg P l ⁻¹	Concentration SRP mg P l ⁻¹	NO ₃ mg N l ⁻¹	Flow average instantaneous m ³ s ⁻¹
N	10.6.88	C	1.96	1.95	6.61	31.7
		G	2.16	1.84	5.76	47.0
	17.6.88	C	2.16	2.04	9.15	15.2
		G	2.12	2.06	8.19	43.0
	24.6.88	C	2.60	2.08	6.89	17.6
		G	2.70	2.30	6.21	43.0
	1.7.88	C	2.56	2.40	6.88	22.2
		G	2.60	2.52	5.70	32.0
	8.7.88	C	2.28	2.28	5.89	26.0
		G	1.82	1.92	6.26	22.5
	15.7.88	C	2.24	2.08	6.21	20.3
		G	2.38	2.24	6.37	28.0
	26.8.88	C	2.80	2.68	7.22	10.7
		G	2.70	2.68	6.72	10.0
	2.9.88	C	2.44	2.32	12.70	15.7
		G	2.40	2.12	8.42	11.0
	9.9.88	C	2.36	2.32	7.91	19.6
		G	2.00	2.04	5.65	8.0
	16.9.88	C	2.72	2.52	4.69	11.0
		G	2.88	2.72	5.37	9.0
	23.9.88	C	3.00	2.88	6.16	11.2
		G	3.20	2.68	6.33	14.0
	29.9.88	C	2.72	2.56	5.65	31.3
		G	2.80	2.56	5.37	43.0
N	22.10.88	C	2.68	2.60	6.52	19.4
		G	2.04	2.00	4.93	24.0
	28.10.88	C	2.36	2.16	15.17	31.5
		G	2.48	2.24	15.17	30.2
	4.11.88	C	2.40	2.28	5.99	34.8
		G	2.48	2.16	15.17	25.4

Appendix B - Continued

Data of collection	Type of sample	Concentration			Flow average instantaneous m ³ s ⁻¹
		TP mg P l ⁻¹	SRP mg P l ⁻¹	NO ₃ mg N l ⁻¹	
11.11.88	C	2.02	2.08	5.99	36.9
	G	2.02	2.24	7.05	24.2
18.11.88	C	2.48	2.36	7.40	33.9
	G	2.80	2.40	8.36	21.8
24.11.88	C	2.74	2.68	7.23	21.9
	G	2.84	2.88	6.70	19.6
30.11.88	C	2.60	2.40	8.22	17.8
	G	2.50	2.40	9.26	36.0
9.12.88	C	2.68	2.40	5.28	39.9
	G	2.00	1.92	9.52	35.4

APPENDIX C - POSSIBLE BIAS IN METHOD 2

Section 3.2 drew attention to the possibility that estimate M_2 may be biased. The difference between its expected value and the true average load M_1 is equal to

$$- \text{cov}(\bar{c}_v, \bar{q})$$

This expression is not identically equal to zero but is difficult to evaluate, because the variables q_i occur both in \bar{c}_v and of course in \bar{q} . However, as both of these terms are averages (albeit weighted in the case of \bar{c}_v) it would be intuitively reasonable to suppose that the size of this term decreases with increasing n and does so roughly in inverse proportion.

For the special case $n = 1$ the value of the above expression is identical to $-\text{cov}(c_i, q_i)$, which is easy to estimate and so may provide an upper bound to the size of the bias term for larger n . Table C therefore lists the estimated values of $\text{cov}(c_i, q_i)$ for the different determinands in the Kingston data and sets them alongside the corresponding values M_1 of load.

It is immediately evident from Table C that the bias of M_2 would be negligible for copper and lead, since the covariance is small in relation to M_1 , without making any allowance for n . In the worst case, that of SRP, the tabulated covariance is 40% of the size of the load. The approximate assumption of proportionately of the bias to $1/n$ would, however, indicate that it would be very much smaller than the errors in M_2 that can arise from sampling (as reflected in the confidence intervals in Table 9). For example, for the load of SRP estimated from weekly data (30 observations) the bias in M_2 would be of the order of 1 tonne per week, whereas the uncertainty due to sampling is of the order of 20-30 tonnes per week.

Table C - Covariance of grab sample concentration with instantaneous flow

Determinand	Load M_1 /tonne week ⁻¹	cov(c_i, q_i)/tonne week ⁻¹
Cd	0.055	-0.0096
Cr	0.19	0.0067
Cu	0.35	0.0070
Pb	0.19	0.0016
Ni	0.24	-0.040
Zn	1.7	0.18
SS	1090	280
TP	52	-17
SRP	45	-18
NO ₃	528	40

APPENDIX D

COMPARISON OF THE FIELLER AND JOLLY METHODS FOR CALCULATING 95% CONFIDENCE LIMITS

Table D1 - Load estimates (tonnes per week) calculated by Method 2 with 95% confidence limits calculated by the Fieller and Jolly methods for weekly, fortnightly, monthly and bimonthly frequency of sampling

		Mean	Lower	Upper	Mean	Lower	Upper	
		Cd				Cr		
Weekly grab	Fieller	0.044	0.036	0.054	0.160	0.130	0.184	
	Jolly	0.044	0.032	0.056	0.160	0.135	0.186	
Fortnightly grab	Fieller	0.041	0.030	0.057	0.150	0.096	0.182	
	Jolly	0.041	0.026	0.056	0.150	0.112	0.188	
Monthly grab	Fieller	0.046	0.016	0.066	0.144	0.032	0.225	
	Jolly	0.046	0.027	0.065	0.144	0.084	0.204	
Bimonthly grab	Fieller	0.035	0.012	0.076	0.090	0.065	0.226	
	Jolly	0.035	0.012	0.058	0.090	0.046	0.134	
		Cu				Pb		
Weekly grab	Fieller	0.292	0.265	0.321	0.152	0.108	0.186	
	Jolly	0.292	0.265	0.319	0.152	0.118	0.186	
Fortnightly grab	Fieller	0.291	0.253	0.343	0.151	0.071	0.195	
	Jolly	0.291	0.247	0.334	0.151	0.105	0.198	
Monthly grab	Fieller	0.321	0.217	0.371	0.140	0.083	0.208	
	Jolly	0.321	0.259	0.383	0.140	0.092	0.188	
Bimonthly grab	Fieller	0.344	0.152	0.413	0.180	0.065	0.253	
	Jolly	0.344	0.266	0.422	0.180	0.114	0.245	
		Ni				Zn		
Weekly grab	Fieller	0.188	0.145	0.247	1.51	1.36	1.62	
	Jolly	0.188	0.145	0.231	1.51	1.37	1.66	
Fortnightly grab	Fieller	0.180	0.129	0.292	1.51	1.29	1.64	
	Jolly	0.180	0.121	0.238	1.51	1.30	1.73	
Monthly grab	Fieller	0.206	0.164	0.258	1.62	1.10	1.84	
	Jolly	0.206	0.160	0.252	1.62	1.32	1.92	
Bimonthly grab	Fieller	0.226	0.151	0.291	1.60	0.80	2.01	
	Jolly	0.226	0.169	0.283	1.60	1.19	2.01	

Table D1 - Continued

		Mean	Lower	Upper	Mean	Lower	Upper	
		SS				TP		
Weekly grab	Fieller	870	430	1140	52	43	69	
	Jolly	870	630	1100	52	40	63	
Fortnightly grab	Fieller	990	0	1430	48	37	96	
	Jolly	990	560	1420	48	27	68	
Monthly grab	Fieller	740	0	1130	42	*	*	
	Jolly	740	400	1080	42	9	75	
Bimonthly grab	Fieller	900	0	1450	40	*	*	
	Jolly	900	230	1570	40	0	99	
		SRP				N03		
Weekly grab	Fieller	46	37	66	354	156	565	
	Jolly	46	34	58	354	122	587	
Fortnightly grab	Fieller	44	32	100	267	192	293	
	Jolly	44	24	64	267	217	317	
Monthly grab	Fieller	38	*	*	280	*	*	
	Jolly	38	4	71	280	194	366	
Bimonthly grab	Fieller	32	*	*	296	*	*	
	Jolly	32	0	94	296	101	491	

* Confidence limits not calculable by Fieller's method
See text: Sections 4.3 and 4.5

• Water Research Centre (1989) plc

The contents of this report are the copyright of the Water Research Centre and all rights are reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted, in any form or by any means electronic, mechanical, photocopying, recording or otherwise, without the prior written consent of WRc.