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Nitrates in surface water, inputs and seasonality

Phase 2

by

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Report Date: July 1988
Report to: Department of the Environment
Contract No: DoE PEC D7/7/136-93/84
FBA Report Ref: RL/T02006-1/1
TFS Project No: T02006-1

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The Freshwater Biological Association is part of the Terrestrial and Freshwater Sciences Directorate of the Natural Environment Research Council.

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SUMMARY

Information on nitrate concentrations and discharge has been collected on the River Frome at East Stoke since 1965, using the same analytical nitrate method so that the results are comparable. These records of weekly spot values of nitrate concentration and daily mean discharges have been analysed for trends and seasonal patterns in both concentration and nitrate loadings.
In this extension of our nitrate contract, a new automated method of intensive sampling has been used to monitor short-term variability and to assess how well similar routine (weekly) sampling schemes can represent the true nitrate record.

(A) Nitrate Concentration

1 The long-term weekly-sampling nitrate record shows that nitrate concentration has been consistently increasing from an annual average of 2.05 mg/l NO_3N in 1965 to 4.41 mg/l in 1987, an average increase of 0.11 mg/l per year.

2 The nitrate concentrations are on average higher in the winter than in the summer and this annual cycle can be described by a cosine wave peaking in early February. The seasonal variation itself has increased over the 23 years as average concentrations have increased.

3 The trend and increasing seasonal periodicity in nitrate concentration can be described by the simple regression model :

$$N = 2.205 + 0.109YR + (0.335 + 0.027\ YR).CW$$

where YR = Time since 1965 = Trend
CW = Cosine((sample week -5)/52)
= Seasonality, peaking in early February.

This equation explains 73.6% of the total variation in nitrate concentration since 1965. It implies that the increase of 2.36 mg/l in annual mean value over the period has been accompanied by an increase in average seasonal variation from 0.66 mg/l in 1965 to 1.86 mg/l in 1987.

Linear trends for each quarter of the year over the period 1965-87 show that nitrate concentration has increased in all seasons of the year but that the increase is greatest in winter. Average summer(July-September) concentration has increased by about 2 mg/l from 1.7 mg/l in 1965, whilst average winter concentrations has increased by about 3 mg/l from 2.4 mg/l in 1965.

4 The River Frome at East Stoke was intensively sampled using the new automated method from July 1987 until April 1988. Where possible a 30 minute sampling frequency was maintained, providing over 8000 values of nitrate concentration. Over the nine-month period the average of the routine weekly sample nitrate values was 4.60 mg/l and the average of all the corresponding days' intensive samples was 4.90 mg/l. The difference of 0.3 mg/l partly represents the small amounts of nitrite in the water which were only measured by the new automated method. The ratio of weekly value to intensive sampling mean never exceeded 1.08, but on one day was only 0.65 - a 35% underestimation.

5 Over the nine-month 30 minute intensive sampling period, the nitrate concentration varied by less than 1 mg/l within 76% of the days.

6 The largest ranges in nitrate concentration within a day were over 2.5 mg/l, equal to about 60% of the day's mean concentration. These large rapid changes in nitrate concentration occurred in October 1987 in response to the first heavy rains after a long dry period. Although there were further periods of heavy rain in November and December 1987, the nitrate concentrations did not fluctuate as widely as in October.

7 In mid-winter, the nitrate concentrations were generally fairly constant at around 5 mg/l, despite large variations in discharge.

(B) Nitrate Load

Nitrate load is a product of nitrate concentration and river discharge.

8 There have been no long-term changes in discharge pattern over the period 1965-1987. The tendency for high concentrations to be be associated with high discharges has not increased over the years. Therefore any increase in nitrate loading is due entirely to increases in nitrate concentration.

9 Examination of the long-term record for the River Frome shows that the coefficient of variation of nitrate concentration within a year (eliminating variation due to long term trend) is only 20% of the mean, whereas for discharge it is 58%. This suggests that even in the River Frome, where flows are fairly stable, the variation in flow causes over 80% of the variability of the nitrate load.
Nitrate loads are consequently much more variable relatively to nitrate concentrations.

10 Because loads are very variable and odd years might dominate any regression equation, a rank correlation test for long-term trend analysis has been included.
There are statistically significant increases in load over the period 1965-1987 for every season except summer (July-September), where the inter-year variation may be masking the smaller increase.

11 Linear regression and rank tests for trend did not reveal any statistically significant trends in the proportion of annual load being transported each season.

12 On average 44% of the nitrate load is transported in the winter period (January -March). In contrast only 11% of the annual load is transported during the summer period (July-September).

13 A simple first-order autoregressive model on the seasonally-adjusted concentrations explains 87.5% of the total nitrate variation, three extra autoregressive terms only explain a further 1.7%.
The concentration at any given time is closely related to the concentration one hour previously and to a lesser extent with the previous day's concentration.
An adequate model of intensive sampling (30 minute behaviour) would involve several terms and better discharge data and is beyond the scope of this report.

CONCLUSIONS

Obviously all river sites and sampling periods can differ in their short term variability of nitrate concentration and loading; being dependent upon upstream catchment characteristics, the rainfall pattern, and the land use, especially with respect to nitrogen inputs. This study was based on the River Frome in Dorset. Its predominantly chalk catchment, gives it a fairly stable discharge of 2-22 m^3s^{-1}, and the chalk aquifer tends to reduce the chemical variability of the river water. Thus the conclusions given below are likely to be understatements of the situation in other similar-sized rivers.

The extent to which concentration can vary within a day influences the accuracy with which single weekly, daily or monthly samples can represent the true nitrate concentration.

1 On the majority of days, nitrate concentration varied by less than 1 mg/l NO_3N.

2 However, heavy rains after a dry spell can lead to nitrate concentrations increasing by 2-3 mg/l over a few hours and then falling back within a short time interval. Such occasions are also likely to give rise to the highest concentrations. Routine weekly or even daily spot sampling is unlikely to detect such short-term peaks.

3 If nitrate concentrations are being monitored for EC water quality regulations it is desirable to have sampling programmes that can measure these short term changes. Automated regular sampling at 1-4 hour intervals could be an effective way forward.
Alternatively an intelligent flexible approach could be used. Weekly sampling is adequate to monitor concentration and estimate load during dry spells at any time of the year. When rain begins and discharge starts changing rapidly, especially after a dry spell, then several samples need to be taken per day.

4 Even in the River Frome where flows are fairly stable, it has been shown that the variation in discharge causes over 80% of the variability of the nitrate load. This is because discharges are relatively more variable than nitrate concentrations.
(The proposed simple approach of assessing the relative contribution to variability in load could be applied to any river.)

5 Nitrate loading is consequently relatively much more variable than nitrate concentration. However because it is more dependent on variation in discharge than nitrate concentration, and the peaks in concentration last for less than a day, monthly and annual loads can still probably be adequately estimated from a daily mean discharge record and one or two nitrate samples per week.

6 Though loads in any one year can be adequately estimated with weekly or twice-weekly nitrate sampling, annual variations in rainfall and hence discharge make it difficult to confidently detect long-term trends in nitrate loadings from just a few years' data.

7 More research is still needed into improving methods for estimating loads. This involves frequency of water chemistry sampling, and how best to combine the concentration data with the best available discharge record.

Two changes in agricultural practise that could effect nitrate loadings and run off are highlighted :

8 There are large increases in acreages of oil seed rape and possibly other vegetable oil crops. (These crops require high applications of nitrogen fertiliser).

9 The increased applications of nitrogen fertiliser to grassland.
In the report from phase 1 of the contract sent to the Department in 1987, conclusion 5 stated that there was a distinct possibility that nitrogen fertiliser applications to Dorset grassland would increase. New information from local farmers shows that in certain cases, because of the milk quota situation, nitrogen fertiliser application has increased. Farmers are tending to cut down on some food concentrates as cattle food, and are using their grass instead. In many cases the farmers are intensifying their grassland management in order to get an extra silage cut.
Whether this situation is occurring nationally is not known, but the Department should be aware of this possibility.
If there was heavy rain in the autumn or late summer these extra fertiliser applications could possibly increase the nitrate run off and leaching from grassland. Very high peaks in nitrate concentration could occur, as found in section 2 above.
Figure 4 from part 1 of the report shows that the fertiliser applications to grassland could double if more of the grassland was intensively farmed.
The Hydrogeology Research Group of the British Geological Survey has recently found high nitrate concentrations building up in groundwater under intensively farmed grassland.

10 If the Department has to make important decisions on restricting the amount of fertiliser usuage in the management of drinking water resources by use of exclusion zones, intensively farmed grassland may be one of the types of agriculture that needs to be restricted.

INTRODUCTION

Changes in management practices and agricultural productivity over the past twenty years have lead to nitrate pollution and eutrophication of lakes and rivers. The annual use of nitrogen fertilisers in the U.K.has increased from just over 0.5 million tonnes per year in 1963 to over 1.5 million tonnes in 1985.
The major problems from nitrate pollution to water management are:

(a) Aquifers provide a large proportion of drinking water resources in England. The water is of high quality and low cost. However nitrate pollution has taken place in many aquifers and is expected to increase further due to the time lapse (up to decades) between increased fertiliser applications and the nitrate reaching the aquifer.
(b) Rivers receive nitrate inputs from both land drainage and sewage effluents and many U.K. rivers have shown a large increase in nitrate concentration over the last twenty years.
(c) Control of nitrate pollution at source is difficult and conventional water treatment does not remove nitrate.
(d) Nitrate levels are set within the EC to 50 mg/l in the EC drinking water directive; but in Anglian, Severn Trent, Thames and Yorkshire water authorities the EC directives have been exceeded, with values up to 80 mg/l being detected.
(e) The capital cost of reducing the high nitrate values down to EC directive levels is estimated at £50million with £5million annual running cost.
(f) One possible method of long term control of nitrate pollution is by the use of exclusion zones, where nitrogen fertiliser applications and the crops grown would be strictly controlled.
(g) In the past it was thought that the major nitrate pollution was from arable farming and that permanent grassland and pasture nitrate run-off was low. However recent work has shown that high values of nitrate can be leached from grass sward grazed by cattle (Ryden et al. 1984)
(h) Nitrogen fertiliser applications to intensively farmed grassland are likely to increase.
(i) Further information on the increased fertiliser applications and the changes in land-use over the past decades was needed to provide data for modelling nitrate increases.

One of the major problems in modelling changes in nitrate concentration and nitrate loading of rivers has been the lack of detailed historic data. The Freshwater Biological Association River Laboratory in Dorset has been investigating chalkstreams since 1965 and has one of the best river nitrate data sets in the U.K. (Casey & Newton 1973, Casey 1975, Casey & Clarke 1979).
This study has therefore been based on the river Frome catchment in Dorset where a long-term record of river nitrates is available.
In addition, an intensive automated nitrate sampling program has been used to examine within-day variation.

OBJECTIVES

To investigate, in a catchment for which earlier nitrate data are available for comparison, seasonality and budgets of nitrate inputs, river concentrations and loads, and their relationship to land use.

CONTRACT PROGRAMME

PHASE 1 (April 1984 - April 1987)

This involved weekly sampling at a series of sites.

In April 1984 sites on the River Frome in Dorset and its main tributaries were selected for sampling for nitrate concentration and also for discharge where suitable. These sites had to be comparable to the sites previously sampled by the Freshwater Biological Association in 1970-71 when discharge and general chemical composition were monitored.
Water sampling and discharge recording also began in April 1984.

During 1984-86 farmers in the River Frome catchment area were contacted to get information on land-use changes and fertiliser applications. MAFF were contacted, both locally and in their Bristol office, to get information on changes in land use from their parish records from 1972 to 1985. MAFF were also asked for information on changes in recommended levels of fertiliser application for different crops.
Wessex Water Authority was contacted to obtain information on the amount of sewage effluent entering the River Frome catchment.
The Fertiliser Manufacturing Association was contacted to get up-to-date information on fertiliser usage and recommendations as some of the data obtained from MAFF were out of date.
An extra sampling site was added on the Tadnoll Brook tributary because the existing site there showed a larger increase in nitrate concentration than in any of the other sampling sites.

Sampling ceased at the end of September 1986. All the data were collated together on NERC's IBM mainframe for statistical analysis and graphical summary.

In April 1987 the final report was completed and sent to DOE.

PHASE 2

A 12 month extension was granted from 1st April 1987 to 31 March 1988. The object of the extension was to limit the sampling to two sites on the River Frome and intensify the sampling regime so that a better understanding of the mechanisms of the nitrate loading could be obtained.
A further three month extension to the end of June 1988 was granted so that the high winter load period could also be included in the report.
1 METHODS AND SAMPLING

A regular weekly nitrate sampling regime had been in operation since 1965 using the same analytical technique. This sampling was continued in exactly the same way to give a direct comparison of current nitrate patterns during this study period with those of the past 20 years.
For this study a new automated sampling and analytical technique has been used. The weekly and automated sample values can be compared at the same site.
The old weekly sampling method measures nitrate concentration only, while the new automated method measures both nitrate and nitrite (Figure 1.1). When tested in the laboratory the nitrite concentration was always less than 0.1 mg N/l.

1.1 Intensive Automated Sampling

The automatic sampler was used in a very intensive sampling regime here at East Stoke on the River Frome at the same spot as the routine weekly sampling program. The main sampling period lasted from July 7th 1987 to April 5th 1988. Samples were usually taken every 30 minutes, especially during high flow events. During periods of expected steady flow sampling was reduced to 6 hour intervals. Another sampling program was set up 20km upstream at Dorchester, but this was much less intensive and more intermittent because of the extra time involved in obtaining samples and supervising the sampling equipment.

1.2 Discharge Records

It has been surprisingly difficult to obtain up to date flow data for the River Frome sampled gauging sites. The national Surface Water Archive has not yet had time to sort out the discharges for 1986 and 1987. Because the River Frome is split at both Dorchester and East Stoke information must be combined from two gauging stations to get the total discharge (and hence nitrate loading) at each of the sampling sites. However, daily mean, minimum and maximum total flows have been obtained directly from Wessex Water Authority (WWA) for the study period up until the end of February 1988. This fortunately includes the high winter flow period. Ideally we would like to have obtained a 30 minute interval record of discharge to compliment the intensive nitrate sampling regime. This would then provide very accurate information on the instantaneous load pattern and its precise relationship with discharge. It would also have enabled us to better compare different frequencies of regular sampling schemes.
At the Dorchester site there are some missing days and only daily mean flows are available. This is the main reason for the less intensive nitrate sampling program at Dorchester.

Because of all the above, this report concentrates on the nitrate record for East Stoke where a complete long term record of daily mean flow was available.

2 RAINFALL

River discharges are obviously at least partly driven by the recent rainfall in the catchment above the river sampling point. Table 2 shows the average pattern of rainfall for all Dorset in 1986 and 1987. The total rainfall in 1986 was 1014 mm (10% above the 1941-70 average of 923 mm), while 1987 was a relative dry year in Dorset (15% below the long term average). More particularly, the monthly rainfall pattern shown in Table 2 gives some indication of how the seasonal rainfall pattern varies between years. For instance October 1987 was nearly twice the October average of 92 mm. Annual variations in rainfall and hence discharge make it difficult to confidently detect trends in nitrate loading from just a few years data.

The rainfall at the East Stoke site was 1032 mm in 1986 and 765 mm in 1987. The daily rainfall at East Stoke during the intensive sampling period is shown in Figures 3.1-3.9 of the next section, where it is superimposed on the daily mean discharges for comparison.

Table 2 Rainfall (mm) in Dorset.

Month	Average 1941-70	Rainfall 1986	% of Average	Rainfall 1987	% of Average
JAN	96	155	161	13	13
FEB	69	8	11	81	123
MAR	64	69	108	85	132
APR	54	71	131	76	143
MAY	67	96	145	23	35
JUN	53	33	62	77	150
JUL	82	68	83	43	52
AUG	79	114	145	23	29
SEP	89	36	40	47	54
OCT	92	86	94	173	189
NOV	107	152	142	79	74
DEC	101	145	145	63	63
Annual	953	1053	108	783	82

3 INTENSIVE AUTOMATIC SAMPLING DATA

3.1 Continuity of Sampling and general variability in concentration

The automatic sampler was in operation from 7th July 1987 to 5th April 1988, a period of 273 days. The initial intention was to take an instantaneous sample every 30 minutes, giving 48 values each day.
The reliability of the equipment to take samples is summarised in Table 3.1 :

TABLE 3.1 Reliability of the continuous sampler equipment in terms of the number of sample values obtained per day over the period 7/7/87 - 5/4/88.

Samples obtained per day	No. of Days	% of Days	
0	22	8	****
1-11	40	15	********
12-23	36	13	*******
24-35	46	17	*********
36-47	36	13	*******
48 (ALL)	93	34	*******************
TOTAL	273	100	

The equipment performed well in general, such that one or more concentration values were obtained for 92% of the days. More importantly, a complete 30 minute interval sampling record was obtained for 34% (93) of the 273 days.

A major aim of the continuous monitoring was to provide information on the variability of nitrate concentration within each day or week. To avoid making incorrect conclusions based on data involving days for which values were only available for a few hours, days were only included in the analyses if one of more values was available for each of at least three of the four 6 hour periods of the day. This gave 198 days for examining short-term variation in nitrate concentration. In fact, all except three of these days had at least 12 sample values. These days are hereafter referred to as 'well-sampled' days.

The frequency distribution of ALL the concentration values obtained over the nine month period, given in Table 3.2, show a range of 2.84 - 6.72 mg/l.
The average concentration during a day was simply calculated as the arithmetic mean of all the available values.
The distribution of the daily means for the 198 'well-sampled' days are shown in Table 3.3. As you would expected the daily means are less variable, ranging from 3.51 to 5.56 mg/l.

Table 3.2 Frequency histogram of all the Nitrate concentration values recorded over the period 8/7/87 - 5/4/88.

(mg N/l)	No. of Days	% of Days	
2.5 - 2.99	1	< 0.1	*
3.0 - 3.49	121	1.5	*
3.5 - 3.99	1457	18	*********
4.0 - 4.49	2434	30	***************
4.5 - 4.99	2435	30	***************
5.0 - 5.49	1466	18	*********
5.5 - 5.99	187	2	*
6.0 - 6.49	19	0.2	*
6.5 - 6.99	2	<0.1	*
TOTAL	8122	100.0	

Table 3.3 Frequency histogram of the daily mean nitrate concentration (mg N/l) for well-sampled days over the period 8/7/87 - 5/4/88.

Daily mean	No. of Days	% of Days	
3.0 - 3.49	0	0	
3.5 - 3.99	37	19	**********
4.0 - 4.49	56	28	**************
4.5 - 4.99	78	39	********************
5.0 - 5.49	26	13	*******
5.5 - 5.99	1	<1	*
6.0 - 6.49	0	0	
TOTAL	198	100	

3.2 Variation in nitrate concentration within each day

The extent to which concentration can vary within a day influences the accuracy with which single daily (or even less frequent) samples can represent the true nitrate record. The within-day variation over the study period July 7th 1987 to April 5th 1988 are summarised in Tables 3.4 - 3.7. For each of the months July 1987-February 1988, for which discharges were available, the 30 minute sample record of nitrate concentration is plotted in figures 3.1-3.8. The routine weekly spot values are superimposed for comparison. For 'well-sampled' days, the estimated nitrate load is plotted as the product of the mean concentration and the mean daily flow, with the daily load estimated from the routine weekly sample superimposed for comparison. On 76% of the days the concentrations varied by less than 1 mg N/l.
The greatest ranges in concentration within a day occurred during October 1987 (Figure 3.4) in response to the first major rains for over three months (figures 3.1-3.3). In October there were three separate days with daily ranges over 2.5 mg N/l (Table 3.5), equal to 57-67% of the days' mean concentrations (Table 3.7). October 1987 was a very wet month, with nearly double the October long-term average rainfall (Table 2). As autumn 1987 passed the nitrate concentration increased by about 1 mg/l (an increase occurs most autumns as explained futher in section 4.2).
Though there were rainy periods with increased flows in both November and December the nitrate concentrations did not fluctuate so widely as in October (figures 3.5,3.6). More importantly, as the flow increased during late January 1988 to fill the river channel, the nitrate concentration remained fairly constant, rarely varying by more than 1 mg N/l (figure 3.8). This almost constant concentration of around 5 mg/l for most of February, despite a widely varying discharge, suggests to us that most of the winter river water is coming from well-mixed groundwater with a fairly constant nitrate concentration. The heavy rain simply increase the hydrostatic pressure on the saturated aquifers, forcing out proportionally more water.
During the first trial sampling period between March 26th and April 9th 1987, after the winter period, an increase of 7 m^3s^{-1} in one day also appeared to have little effect on concentration (figure 3.9).
Overall, days with higher average concentration were not necessarily more variable (figure 3.10).

Obviously, all periods and sites can differ in their short-term variability of nitrate concentration, being dependent upon the upstream catchment characteristics, the particular rainfall pattern over the study period and the land uses especially with respect to nitrogen inputs. However, this study supports the view that the highest concentrations occur during the first rains after a long dry spell. This agrees with our experience from the long-term weekly sampling of nitrates in the River Frome(Dorset) and elsewhere, most notably following the drought of 1976. The study also suggests that for lower catchment sites on rivers like the Dorset Frome, the first rains after a long dry spell lead to river nitrate concentration increasing by 2-3 mg N/l over a few hours and then falling back within a few more hours (figure 3.11). This suggests that at such times it is desirable to have much more frequent sampling for monitoring nitrate concentration, especially if the nitrate concentration is being monitored for EC water quality regulations. However, the river discharge is not usually high during such first rains. Hence the nitrate loading passing down the river is not usually as great as during the periods of high winter flow.

The nitrate concentrations seem to be less variable during the high flow winter period than during the autumn, even though the winter flows are themselves very variable and may change rapidly. It would be interesting to know whether the winter concentrations have less short-term variability now than in past years, and if so whether this is related to changes in farming practices. Casey (1975) sampled nitrate concentration hourly during a series of storm events lasting seven days in December 1972 when discharge varied from 5 to 13 $m^3 s^{-1}$. He found that nitrate concentration varied from 1-3 mg/l, a range of 2 mg/l which was relatively large compared to the average concentration level in 1972. Though the average concentration has increased considerably since 1972, from the present evidence the variability in concentration over a few days during winter rains has not increased.

Table 3.4 Frequency histogram of the within-day standard deviation of nitrate concentration (mg N/l) for well-sampled days over the period 8/7/87 - 5/4/88.

Standard Deviation	No. of Days	% of Days	
0.0 - 0.09	66	33.3	*****************
0.1 - 0.19	73	36.9	*******************
0.2 - 0.29	37	18.7	**********
0.3 - 0.39	11	5.6	***
0.4 - 0.49	4	2.0	*
0.5 - 0.59	5	2.5	**
0.6 - 0.69	0	0.0	
0.7 - 0.79	1	0.5	*
0.8 - 0.89	0	0.0	
0.9 - 0.99	1	0.5	*
TOTAL	198	100.0	

Table 3.5 Frequency histogram of the range of nitrate concentration (mg N/l) within well-sampled days over the period 8/7/87 - 5/4/88.

Daily Range	No. of Days	% of Days	
0.0 - 0.49	76	38.4	********************
0.5 - 0.99	75	37.9	*******************
1.0 - 1.49	31	15.7	********
1.5 - 1.99	10	5.0	*****
2.0 - 2.49	3	1.5	*
2.5 - 2.99	3	1.5	*
TOTAL	198	100.0	

Table 3.6 Frequency histogram of the within-day percentage coefficient of variation of nitrate concentrations for the well-sampled days over the period 8/7/87 - 5/4/88.

% C.V.	No. of Days	% of Days	
0 - 1.9	58	29.3	***************
2 - 3.9	69	34.9	******************
4 - 5.9	37	18.7	**********
6 - 7.9	18	9.1	*****
8 - 9.9	7	3.5	****
10 - 11.9	4	2.0	*
12 - 13.9	3	1.5	*
14 - 15.9	0	0.0	
16 - 17.9	1	0.5	*
18 - 19.9	1	0.5	*
TOTAL	198	100.0	

Table 3.7 Frequency histogram of the daily range of nitrate concentration (mg N/l).

% Range	No. of Days	% of Days	
0 - 9.9	68	34.3	*****************
10 - 19.9	75	37.9	*******************
20 - 29.9	28	14.1	********
30 - 39.9	19	9.6	*****
40 - 49.9	5	2.5	**
50 - 59.9	1	0.5	*
60 - 69.9	2	1.0	*
TOTAL	198	100.0	

Figure 3.1 July 1987 : Plot of the 30 minute automatic sampling record of total organic nitrogen (nitrate + nitrite) TON mg/l (top diagram) ; daily mean discharge ($m^3 s^{-1}$) and daily rainfall (mm) (middle) ; and daily TON load (tonnes) (bottom).
⊛ denotes the routine weekly spot values of nitrate concentration and estimated daily loads for comparison.

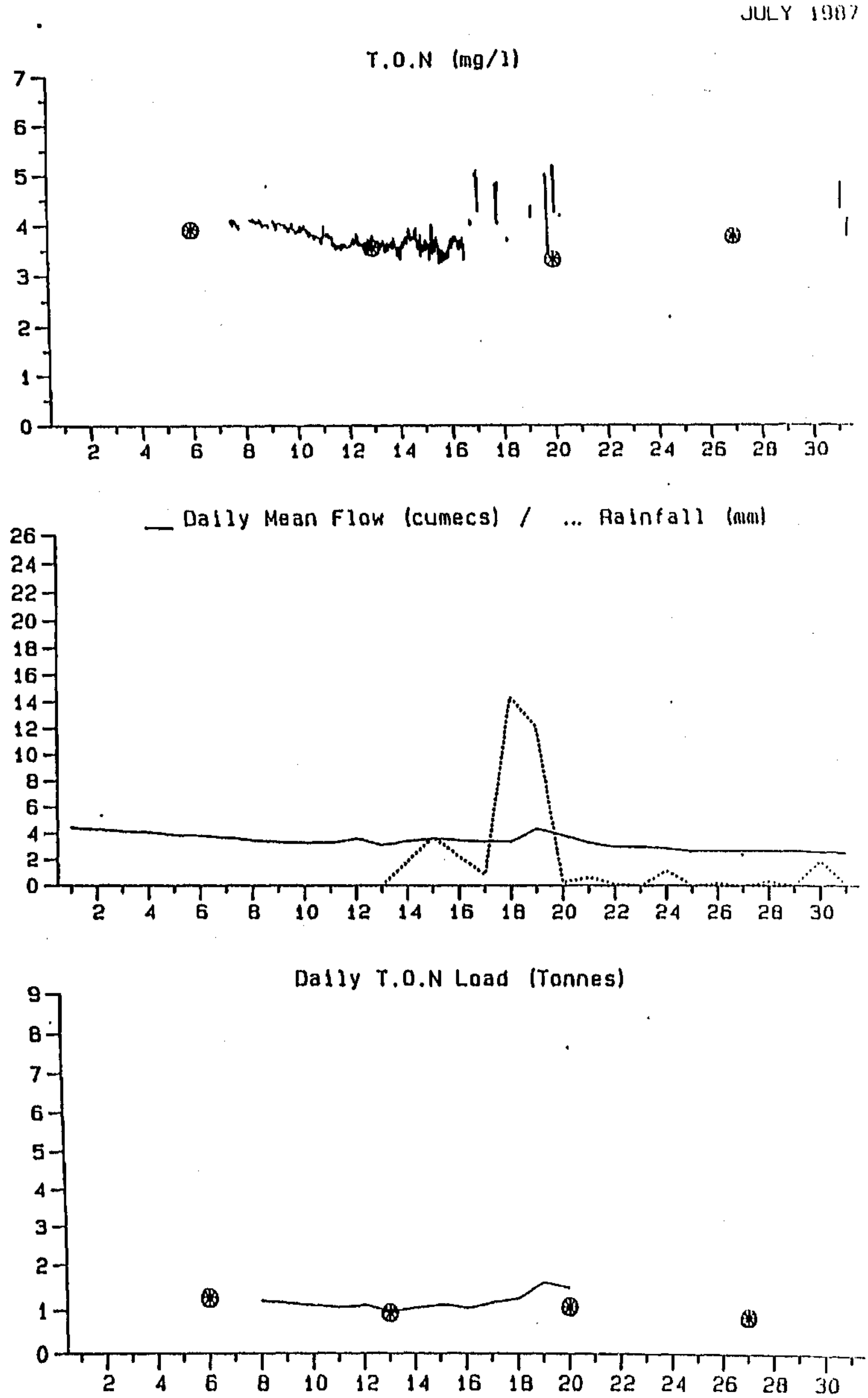


Figure 3.2 August 1987 : see Figure 3.1 for details.

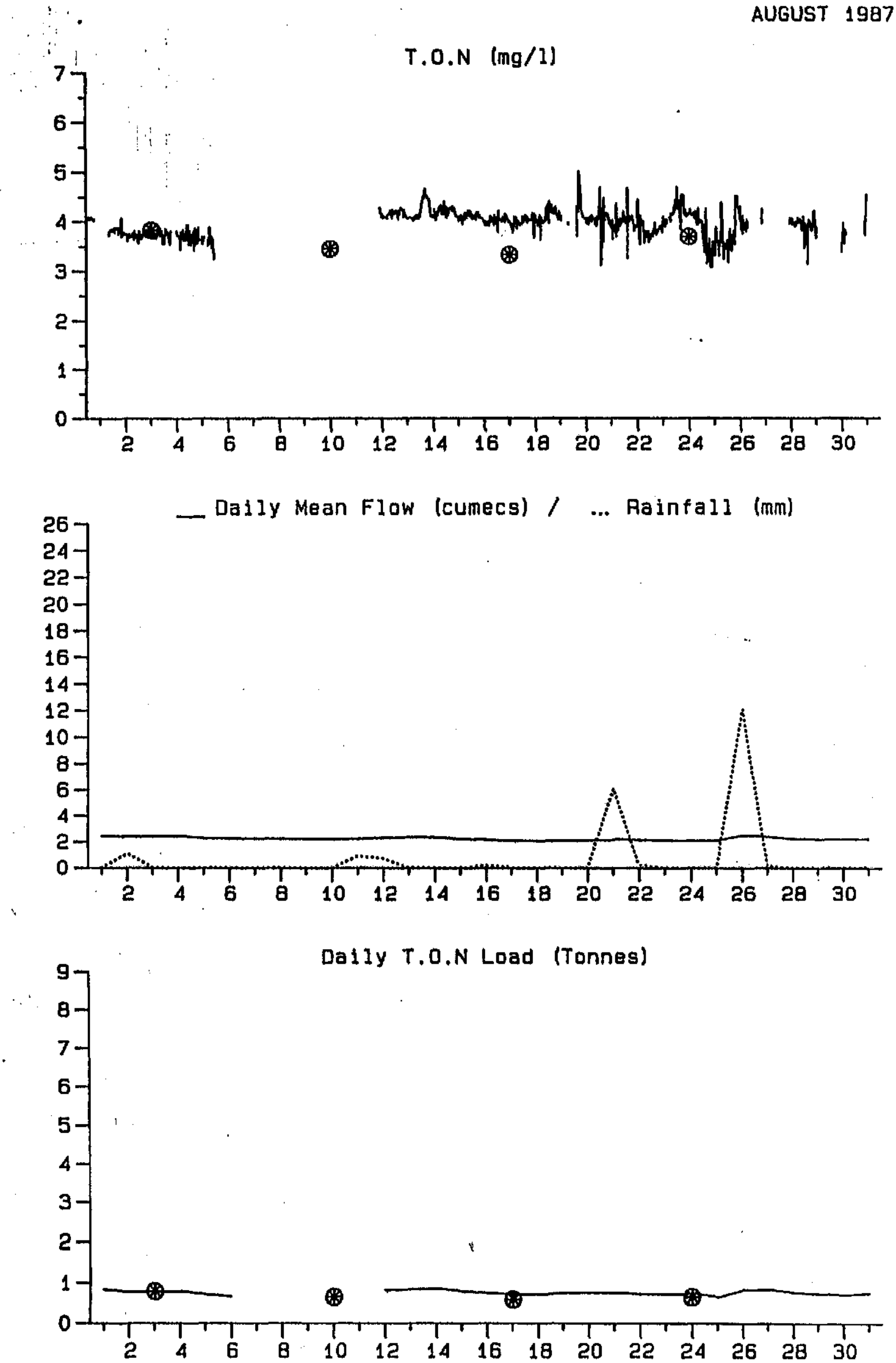


Figure 3.3 September 1987 : see Figure 3.1 for details.

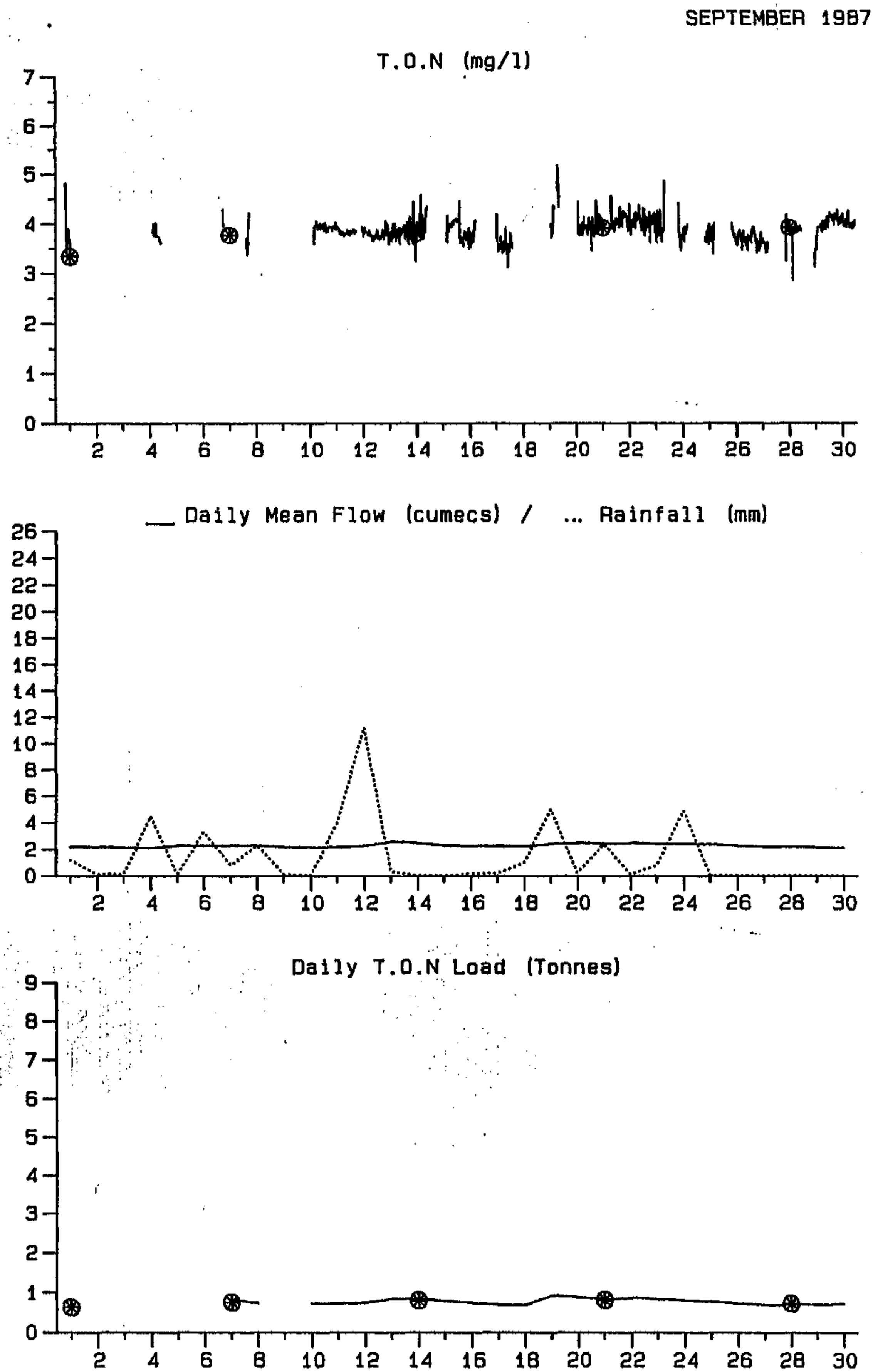


Figure 3.4 October 1987 : see Figure 3.1 for details.

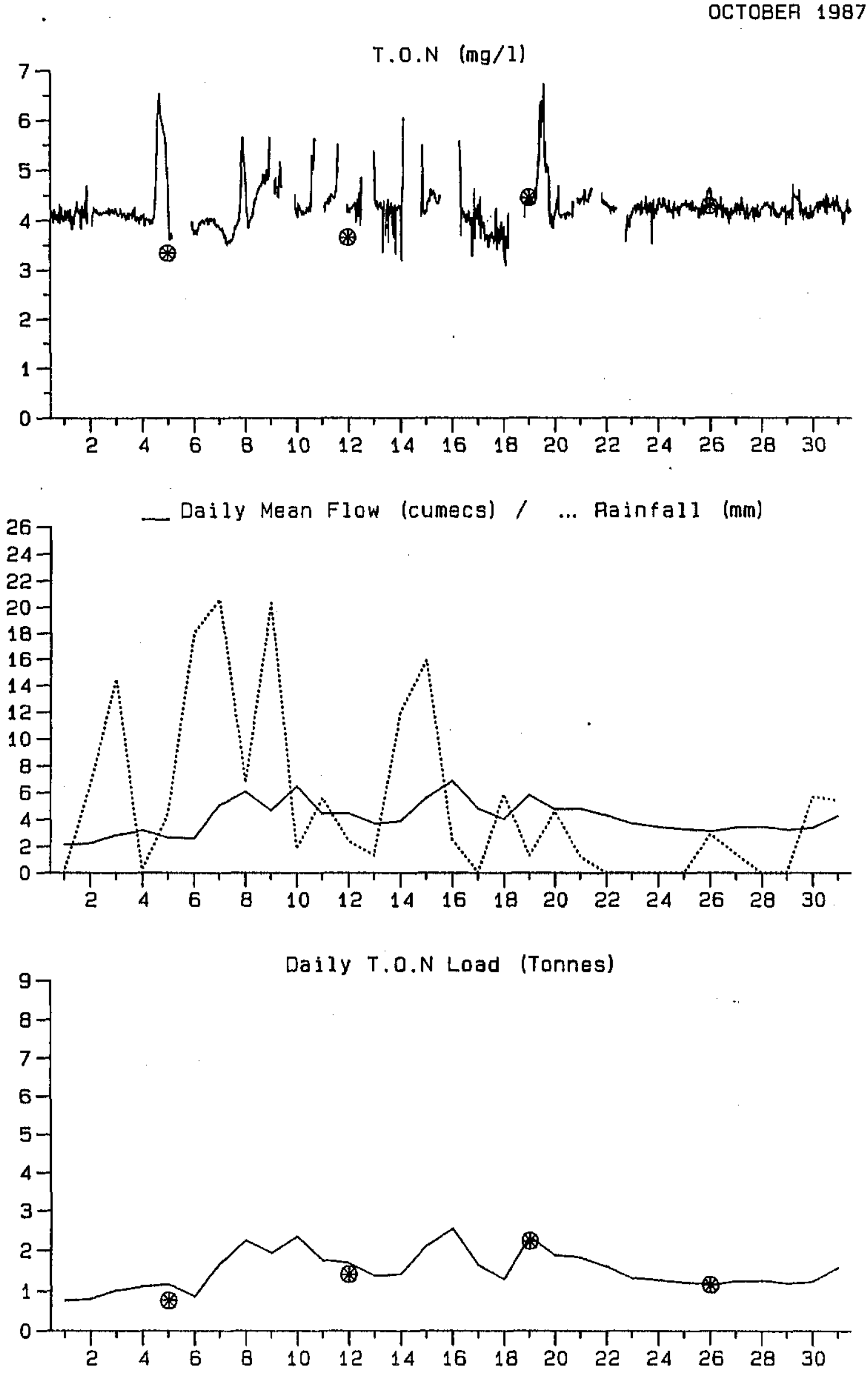


Figure 3.5 November 1987 : see Figure 3.1 for details.

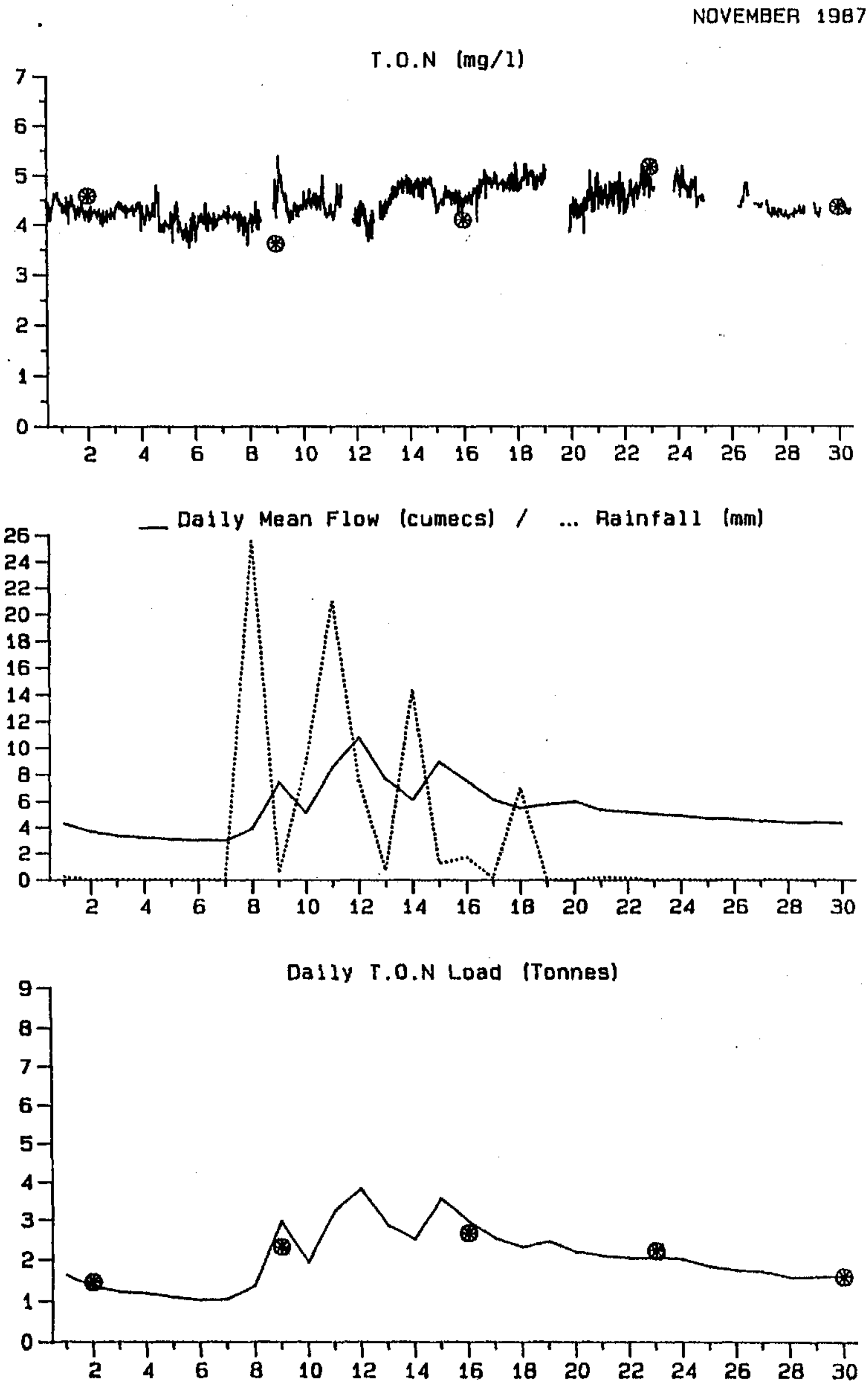


Figure 3.6 December 1987 : see Figure 3.1 for details.

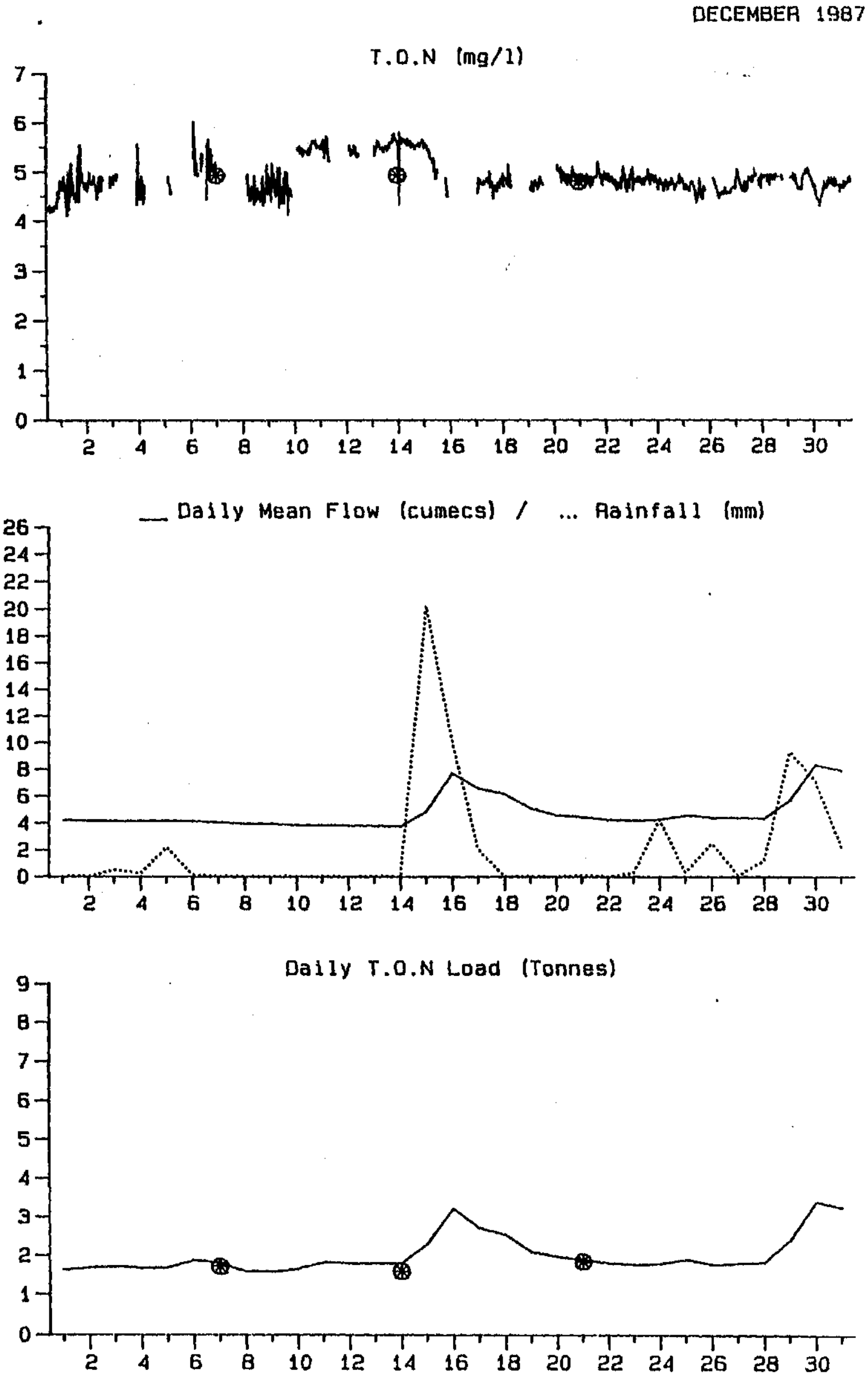


Figure 3.7 January 1988 : see Figure 3.1 for details.

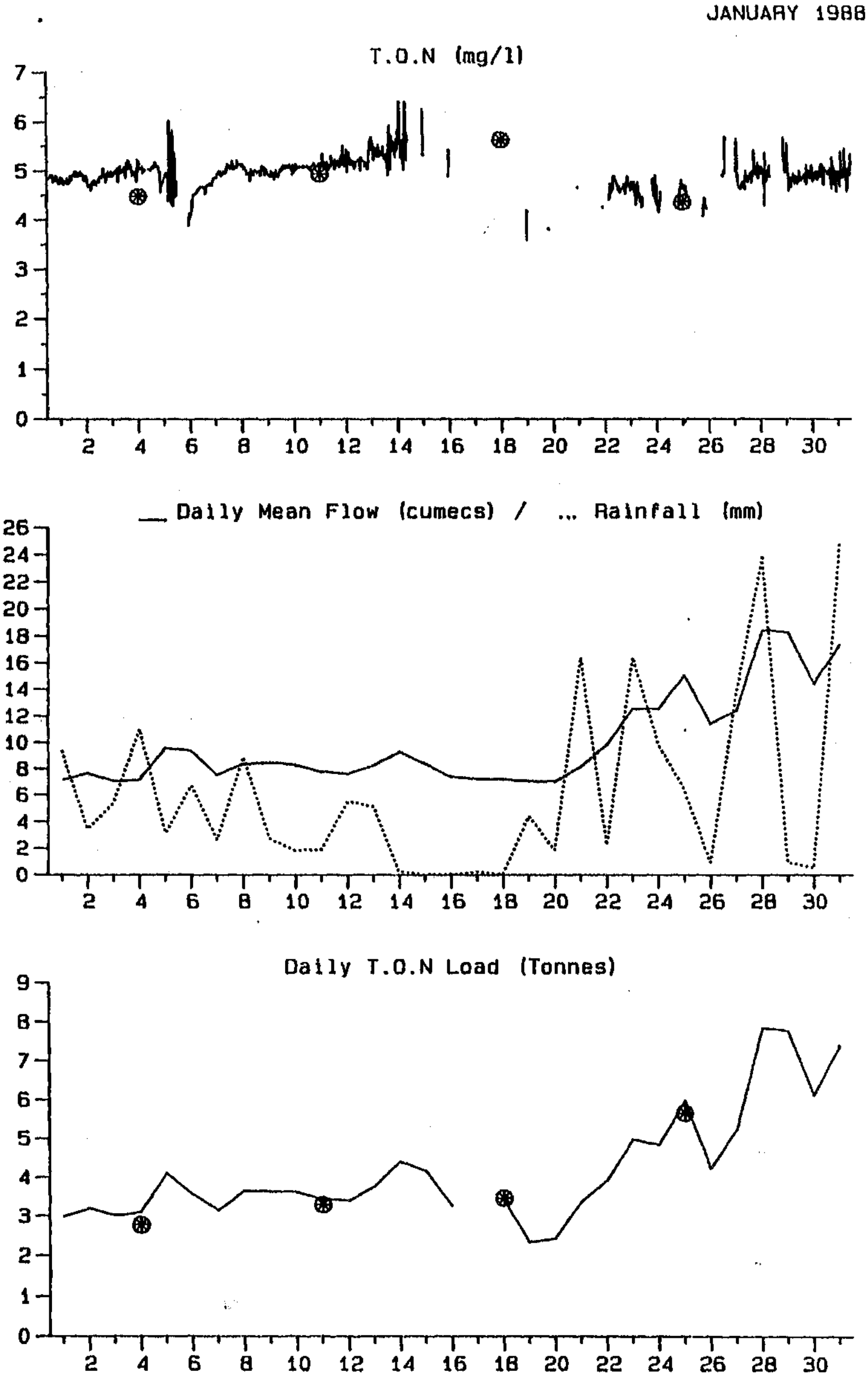


Figure 3.8 February 1988 : see Figure 3.1 for details.

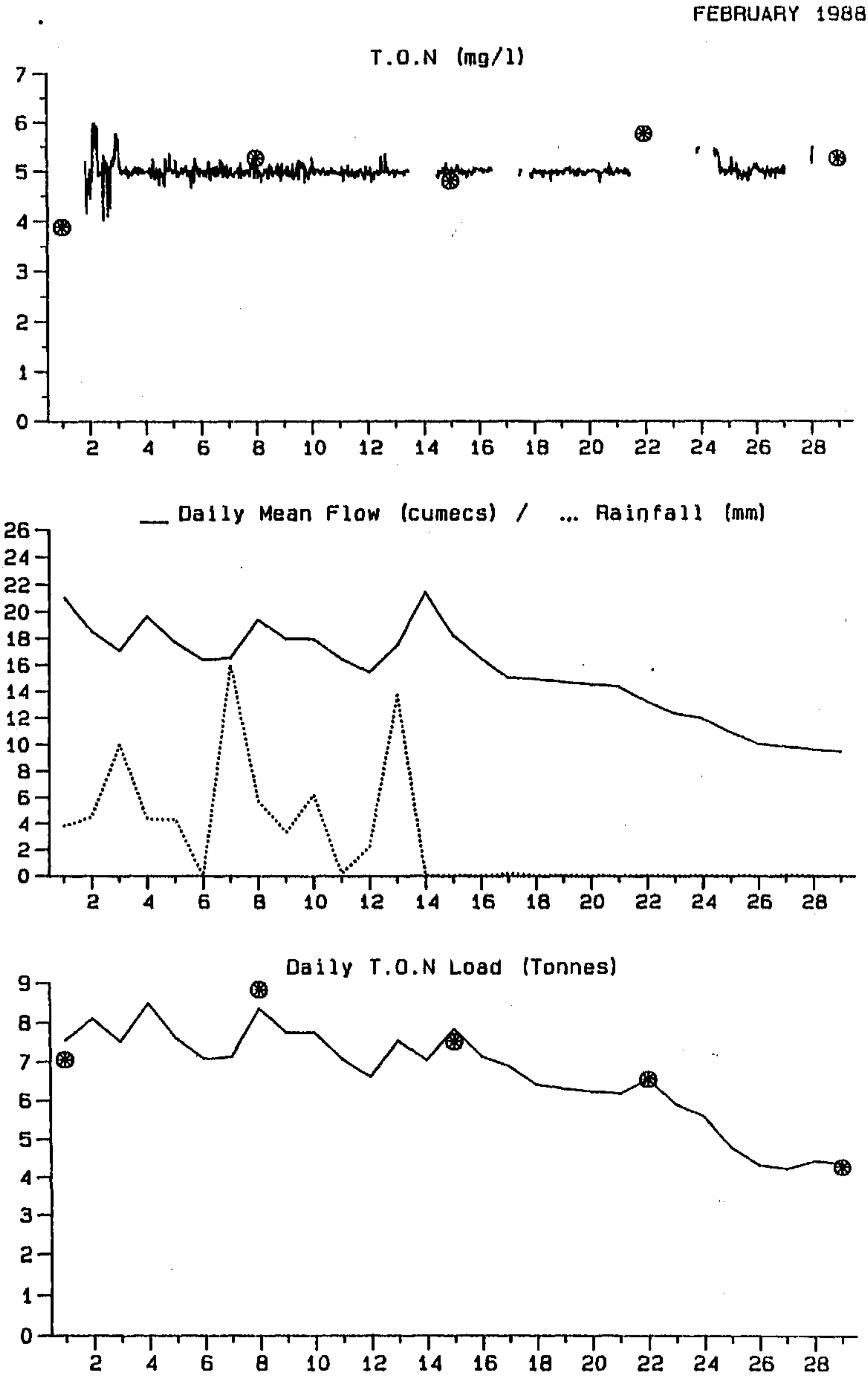


Figure 3.9 March 26th - April 9th 1987 :
see Figure 3.1 for details.

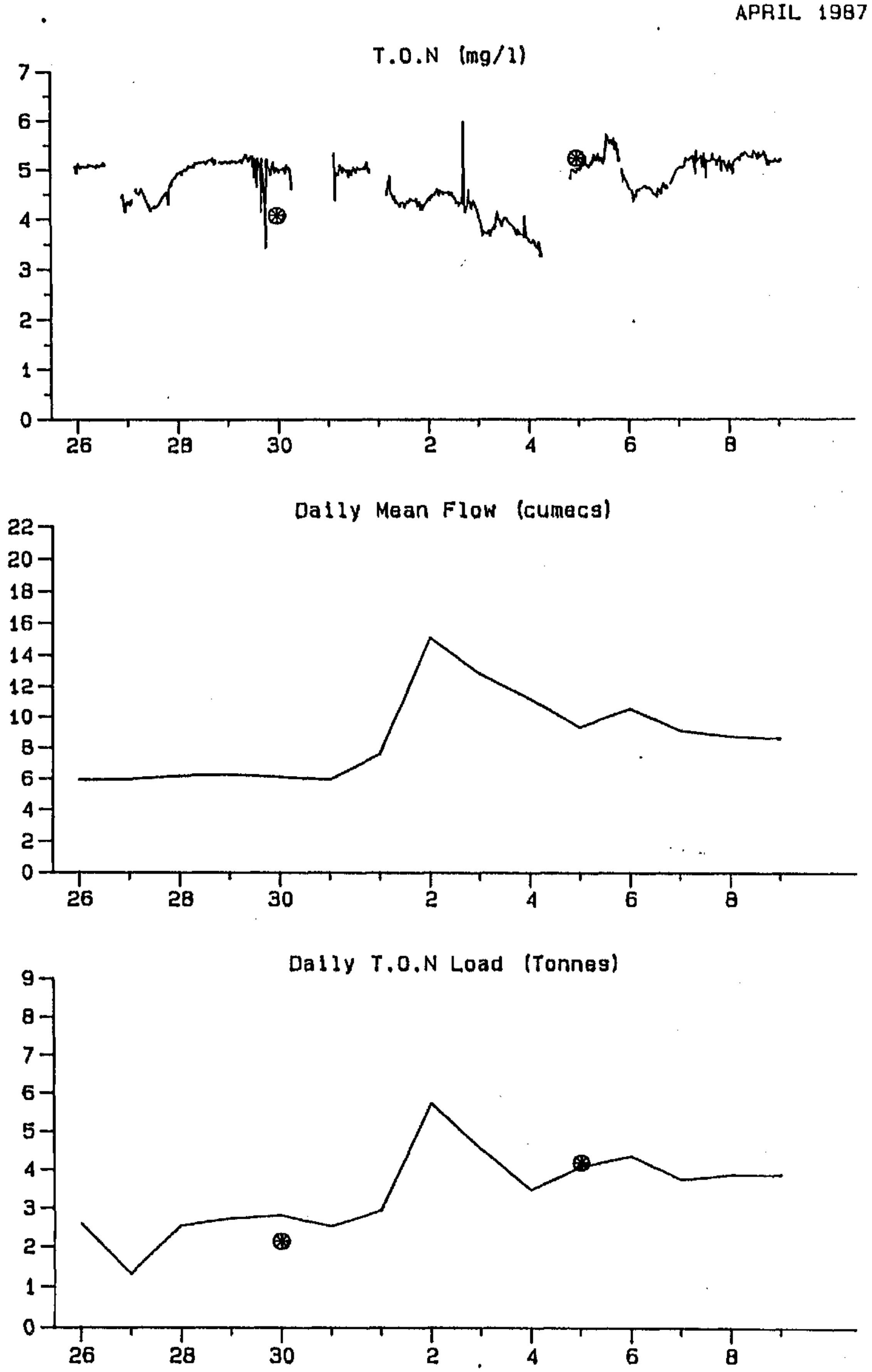


Figure 3.10 Standard deviation of nitrate concentration within a day plotted against the day's mean concentration.
Based on 30 minute automated sampling of the River Frome at East Stoke (Dorset) : July 1987 - April 1988.
Digits denote number of co-incident observations.

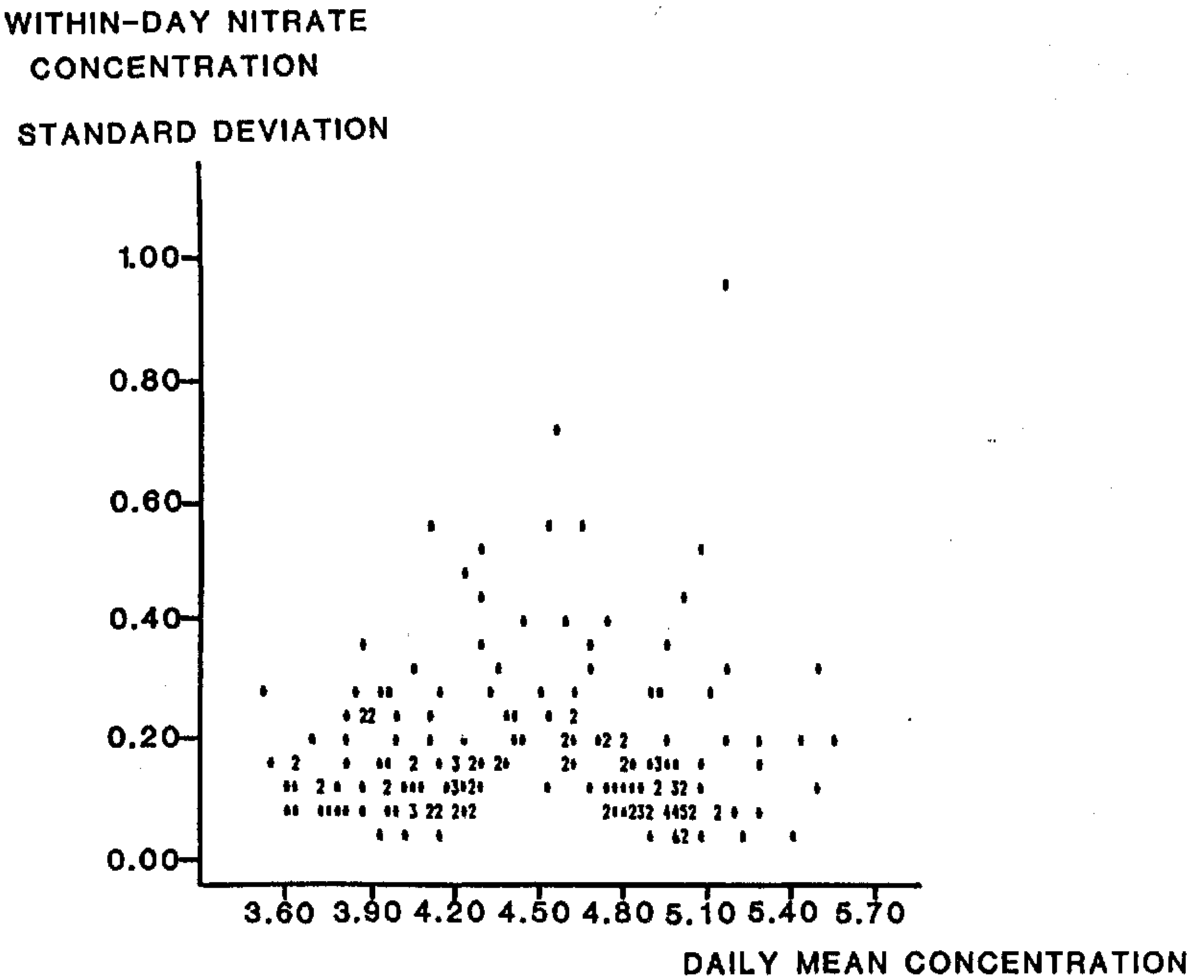


Figure 3.11 Changes in nitrates with discharge during first rains in October 1987 following a long dry spell.
See figure 3.1 for details.

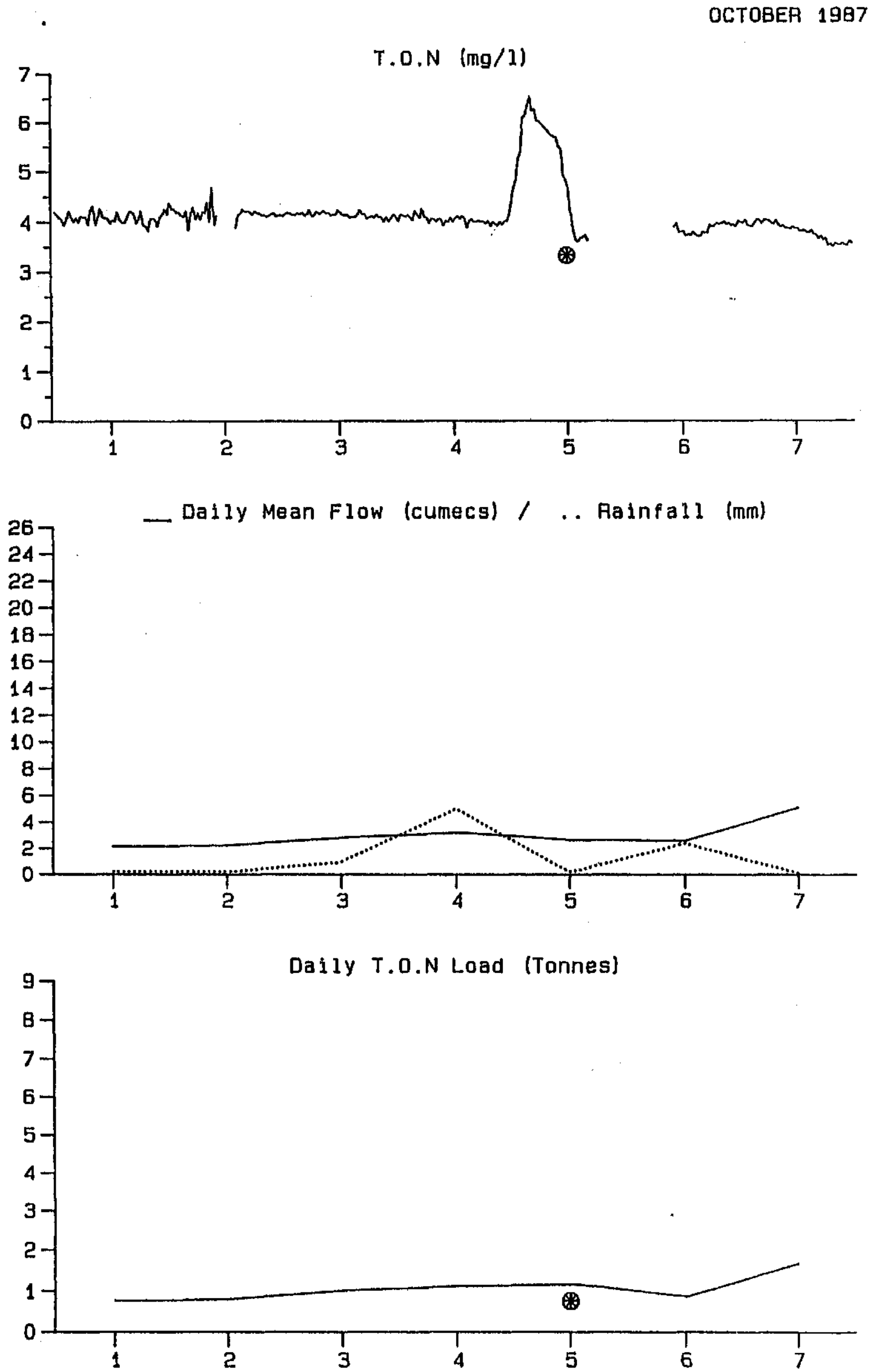
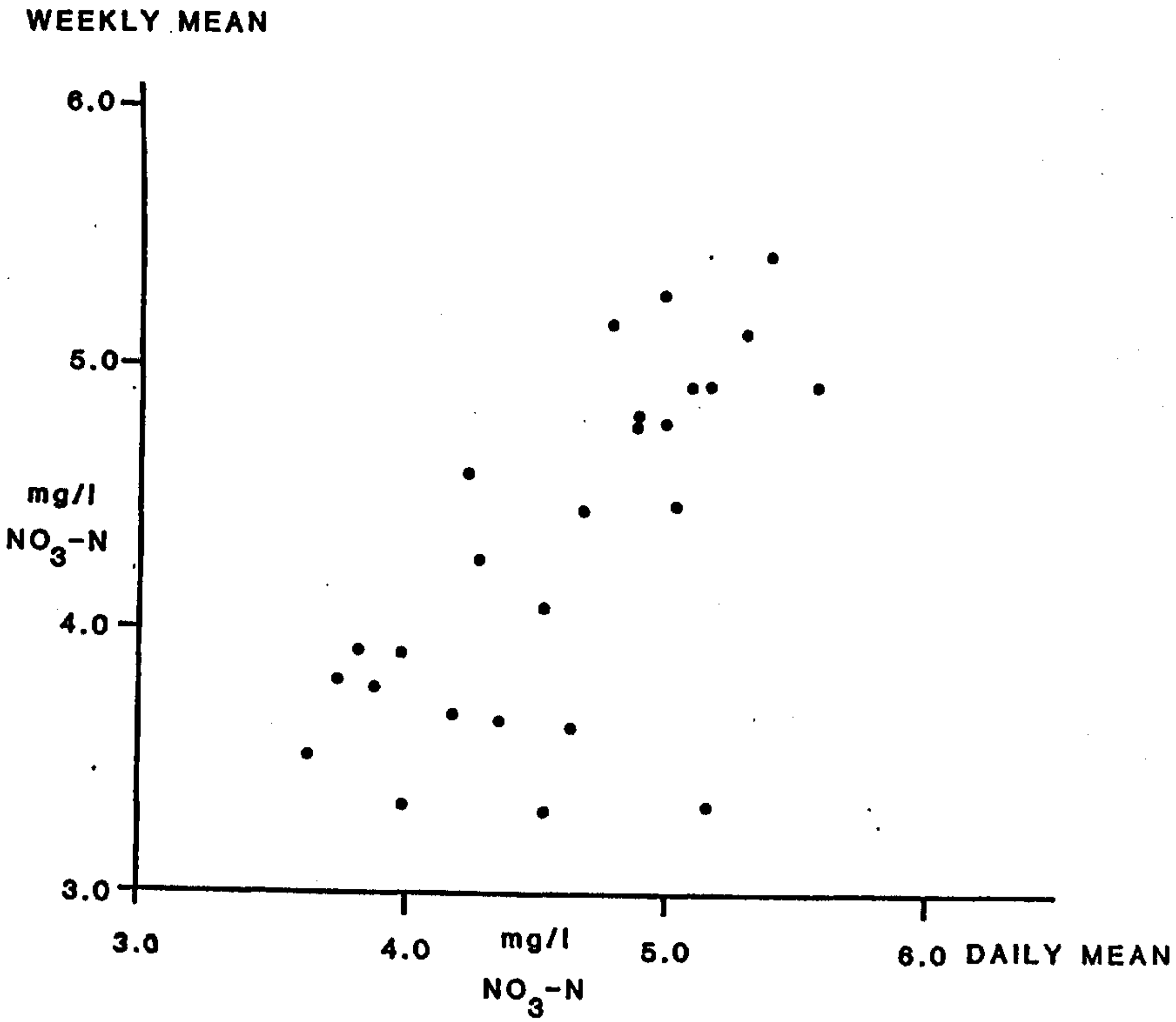


Figure 3.12 Plot of spot weekly nitrate sample value against the day's mean calculated from the 30 minute automatic sampler, for 'well-sampled' days.



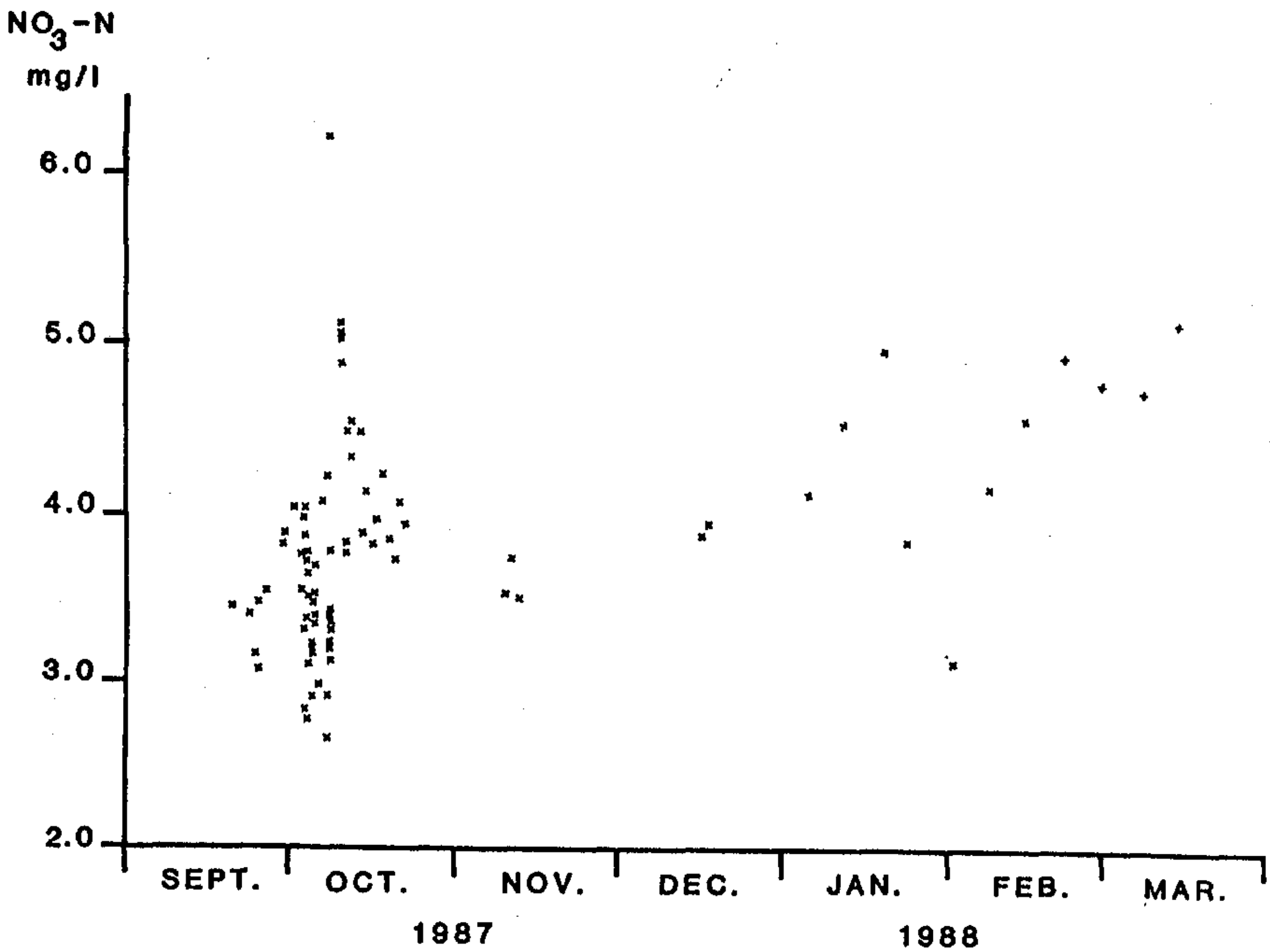
3.3 Comparison with the routine weekly spot nitrate sampling

It is important to know how well a routine weekly spot sample can adequate represent the true nitrate concentration record. Over the period of continuous monitoring, there were 26 occasions when the weekly spot value occurred on a day which was 'well-sampled' (figure 3.12). The average of the weekly values was 4.60 mg N/l. This was 0.30 mg N/l less than the average of the values using the continuous sampler. Though the continuous sampler measured nitrite as well as nitrate, nitrite was found in tests to never exceed 0.1 mg N/l at 4 mg NO_3 N/l. The remaining difference probably results from differences in the analytical chemical methods used. The ratio of weekly value to continuous sampler mean never exceeded 1.08, but on one occasion was only 0.65 - a 35% underestimation.

3.4 Automatic sampling at the Dorchester site

Because the Dorchester site was further away and hence required more effort to collect samples and maintain the equipment, far fewer samples were obtained than at the East Stoke.
The samples obtained showed a similar pattern to the samples taken at East Stoke, with the October nitrate values showing the most variation (Figure 3.13). The heavy rainfall on the 2nd and 3rd of October increased the discharge from 0.95 to 1.43 m^3s^{-1} and the nitrate concentration decreased from 4.00 to 2.82 mg l^{-1} before rising again to 3.47 mg l^{-1} by the early hours of October 4th. This remained steady for about eight hours before decreasing steadily to 2.97 mg.l^{-1} by October 5th. More heavy rain on the 6th and 7th increased the discharge up to 3.56 m^3s^{-1} with nitrate concentration changing from 4.08 down to 2.66 and back up to 4.23 mg l^{-1}. By 7am on October 8th nitrates reached a peak of 6.22 mg l^{-1} before falling back to 5.11 by October 9th and 3.84 mg l^{-1} by the 10th. More rain on the 11th caused a smaller rapid rise and fall back, after which concentration remained between 3.5 and 4.0 mg l^{-1} for the rest of the year. Those few concentrations obtained during January and February 1988 varied between 3.8 and 5.0 mg l^{-1}, apart from a value of 3.12 following heavy rain at the end of January.

Figure 3.13 Automatic sampler values of nitrate concentration obtained from Dorchester on the River Frome (Dorset) between April 1987 and April 1988.



4 ANALYSIS OF THE LONG-TERM CHANGES IN NITRATE PATTERN IN THE RIVER FROME AT EAST STOKE, DORSET.

At East Stoke a weekly nitrate sample has been taken by the FBA since 1965, and daily mean discharges at the same spot are available from Wessex Water Authority since 1966. This section gives some simple results of our analysis of this long-term record.

4.1 Long-term Trend in Nitrate Concentration

The steady long-term increase in nitrate concentration in the River Frome at East Stoke is clearly shown in Figure 4.1 and Table 4.1. The average nitrate concentration has risen from 2.05 mg/l in 1965 to 4.41 mg/l in 1987. This represents a average increase of 0.11 mg/l per year. Given that only 52 weekly spot samples are taken each year and hence the potential sampling error, the estimated yearly means show a surprisingly linear increase. There is no evidence that this increase is changing pace.

Table 4.1 Yearly statistics for weekly sampled nitrate concentration (mg/l) in the River Frome at East Stoke, Dorset.

Year	Mean	S.E.	Minimum	Maximum
1965	2.05	0.06	1.14	3.00
1966	2.42	0.07	1.34	3.46
1967	2.31	0.06	1.39	3.40
1968	2.34	0.07	1.17	3.51
1969	2.76	0.06	1.58	3.50
1970	2.98	0.06	2.15	4.30
1971	2.89	0.07	2.20	4.10
1972	3.06	0.07	2.21	4.32
1973	2.80	0.06	2.03	3.68
1974	3.12	0.09	2.00	4.56
1975	3.28	0.08	2.32	4.70
1976	3.44	0.18	1.50	7.24
1977	3.75	0.10	2.38	5.20
1978	3.58	0.08	2.20	5.30
1979	3.87	0.08	2.95	5.86
1980	3.67	0.08	2.62	4.86
1981	4.02	0.09	2.49	5.69
1982	4.06	0.11	2.31	5.57
1983	4.18	0.11	2.37	5.76
1984	4.28	0.14	2.19	6.13
1985	4.32	0.12	2.69	5.96
1986	4.50	0.12	2.77	6.25
1987	4.41	0.09	3.30	5.60

4.2 Overall Seasonal Pattern of Nitrate Concentration

As a means of showing the seasonal pattern in nitrate concentration, Figure 4.1 also shows the mean,standard error, minimum and maximum concentration for each of the weeks (1-52) of the year, averaged over the period 1965-87. As is common with nitrates the concentrations are on average higher in winter and lowest in mid-summer. This periodic cycle in concentration is well described by a cosine wave peaking in early February. This averaged seasonal cycle has an amplitude or range of about 1.3 mg/l.

4.3 Simple Model describing the Trend and Seasonality

The trend and seasonal periodicity in nitrate concentration described above can be summarised by the following simple regression model, as used by Casey and Clarke(1979) :

$$N = \underset{(0.030)}{2.206} + \underset{(0.002)}{0.109}\,YR + \underset{(0.022)}{0.626}\,CW \qquad \text{(Eq 4.1)}$$

where YR = Time since 1965 (Years) = "Trend"
CW = Cosine((sample week -5)/52)
= "seasonality" peaking in early February (week 5)
and standard errors of coefficients are given in brackets.

These two deterministic components jointly explain 72.1% of the nitrate variation since 1965. However, it seems likely that as nitrate levels have risen so the amount of seasonal variation will also increase. To assess this , an extra term CWYR was added to equation (4.1) to represent the extent to which the seasonal variation increased with the trend.

Defining CWYR=CW x YR , led to a second descriptive model :

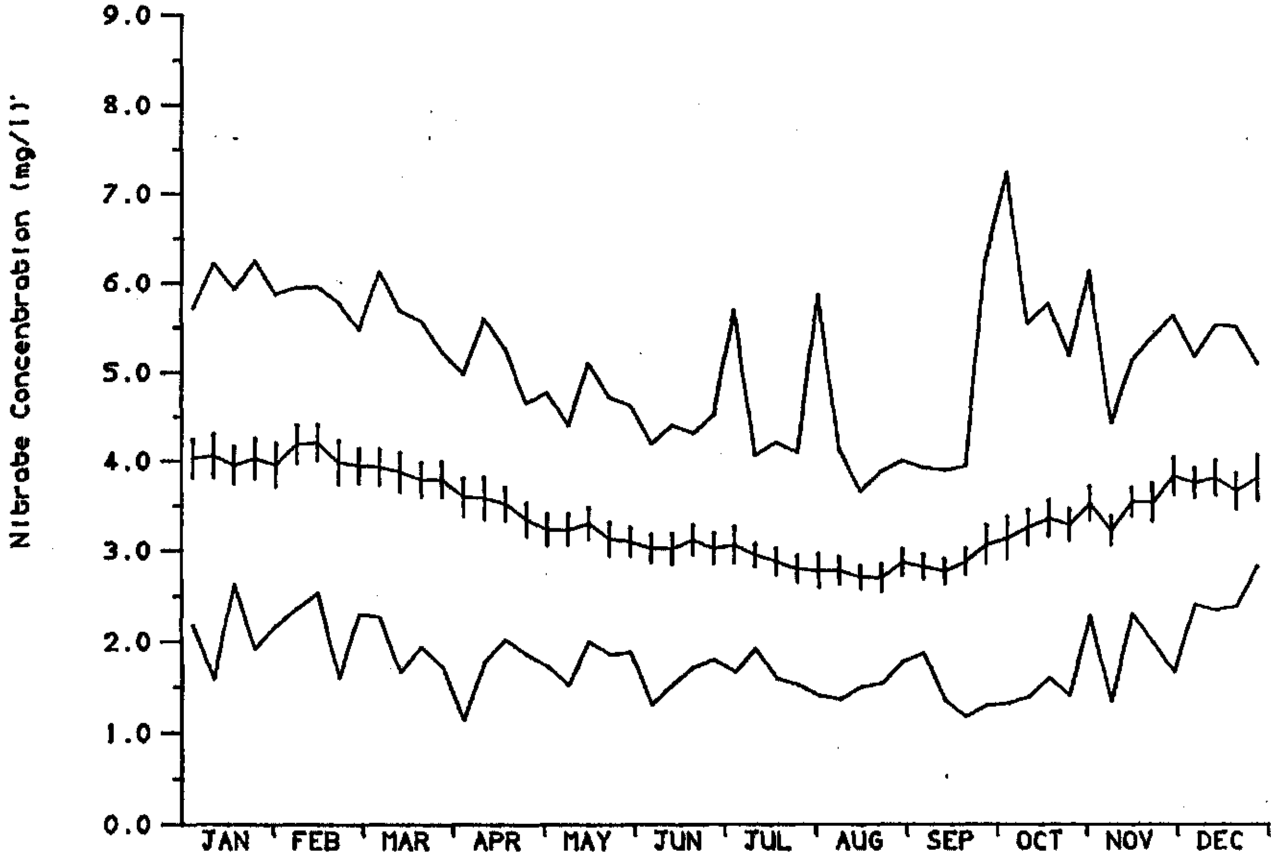
$$N = \underset{(0.029)}{2.205} + \underset{(0.002)}{0.109}\,YR + \underset{(0.041)}{0.335}\,CW + \underset{(0.003)}{0.027}\,CWYR \qquad \text{(Eq 4.2)}$$

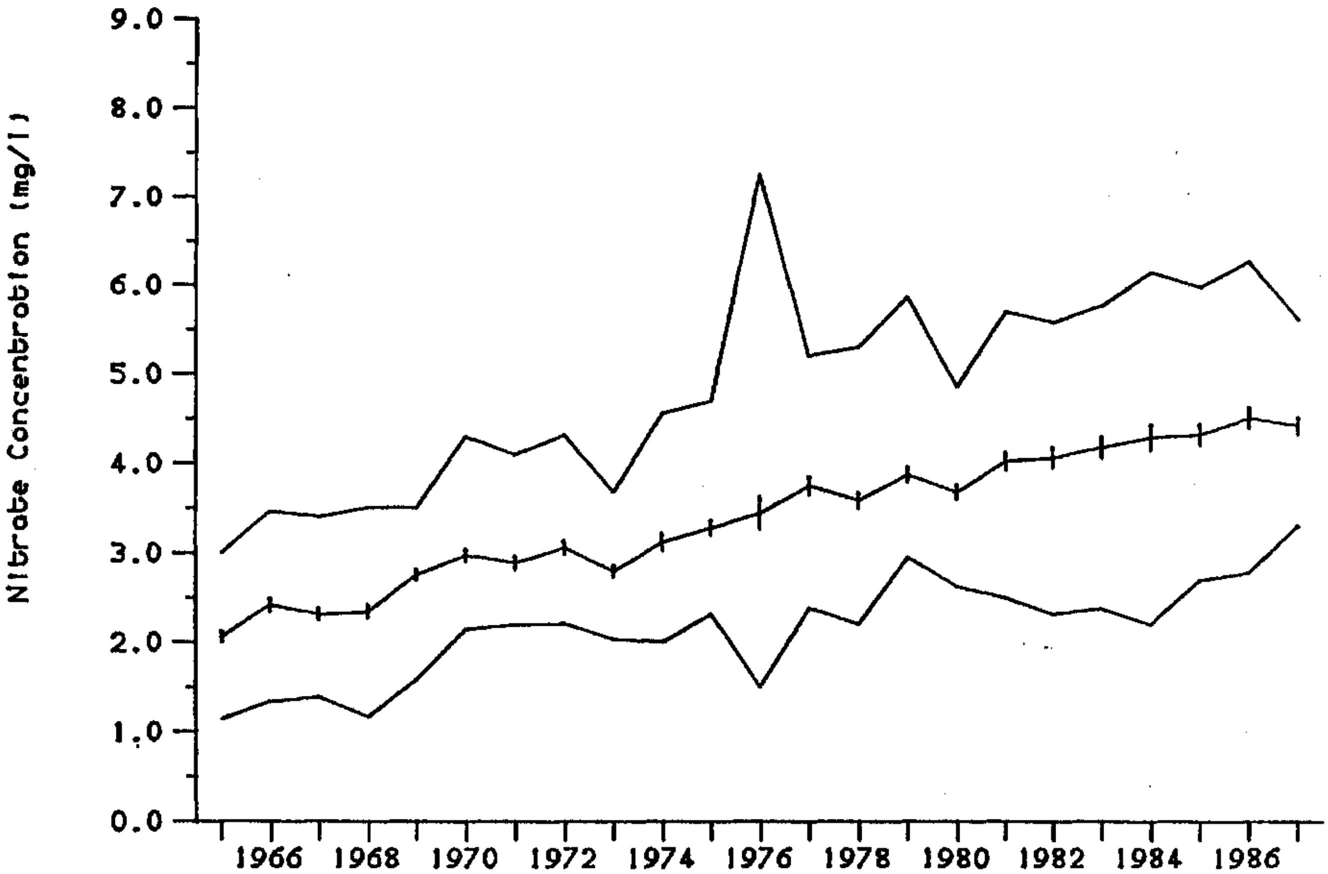
which explained 73.6% of the total variation.
This can be re-expressed as :

$$N = 2.205 + 0.109\,YR + (0.335 + 0.027\,YR)\,CW \qquad \text{(Eq 4.3)}$$

If this model holds, it implies that the smoothed seasonal variation within a year has increased from 0.33 mg/l in 1965 to about 0.93 mg/l by 1987. Thus the increase of 2.36 mg/l in annual mean over the period has been partially complimented by an increase in averaged seasonal variation of 0.6 mg/l.

Figure 4.1 (A) Seasonal and (B) Annual summary statistics for nitrate concentration (mg/l) in the River Frome at East Stoke (Dorset) over the period 1965-87. For each year, and each week (1-52) of the year, the mean, minimum and maximum values are shown. Vertical bars denote ±1 standard errors.





4.4 <u>Changes in Seasonal Pattern of Nitrate Concentration</u>

The descriptive model equation (4.3) suggests the seasonal pattern of nitrate concentration may have changed over the period, perhaps due to changes in farming practice and timing of fertiliser application.
To examine this, Table 4.2 and Figure 4.2 show the change in three-monthly mean nitrate concentration over the period 1965-1987.

The linear trends for each quarter separately, given in Table 4.3, show that nitrate concentration has increased in all seasons of the year, but the increase is greatest in winter. Average summer (July-September) concentration has increased by about 2 mg/l from 1.7 mg/l in 1965, while average winter (January-March) concentration has increased by about 3 mg/l from 2.4 mg/l in 1965.

Table 4.2 Quarterly means of nitrate concentration (mg/l) in the River Frome at East Stoke over the period 1965-87.

Year	JAN-MAR	APR-JUN	JUL-SEP	OCT-DEC	Annual mean
1965	2.39	1.84	1.70	2.29	2.05
1966	2.74	2.40	2.03	2.46	2.42
1967	2.68	2.14	1.99	2.44	2.31
1968	2.70	1.96	1.95	2.77	2.34
1969	3.09	2.64	2.53	2.77	2.76
1970	3.19	2.97	2.60	3.14	2.98
1971	3.51	2.71	2.48	2.84	2.89
1972	3.70	2.86	2.66	3.01	3.06
1973	3.40	2.54	2.35	2.91	2.80
1974	3.72	2.91	2.51	3.35	3.12
1975	3.67	3.03	2.82	3.62	3.28
1976	3.74	2.70	2.38	5.05	3.44
1977	4.64	3.75	3.29	3.26	3.75
1978	4.22	3.61	3.10	3.37	3.58
1979	4.21	3.99	3.76	3.49	3.87
1980	4.16	3.79	3.02	3.71	3.67
1981	4.58	3.97	3.41	4.13	4.02
1982	5.00	4.12	3.24	3.86	4.06
1983	4.84	3.66	3.64	4.59	4.18
1984	5.44	3.86	3.23	4.54	4.28
1985	5.26	4.26	3.39	4.36	4.32
1986	5.62	4.23	3.69	4.45	4.50
1987	4.98	4.67	3.65	4.34	4.41

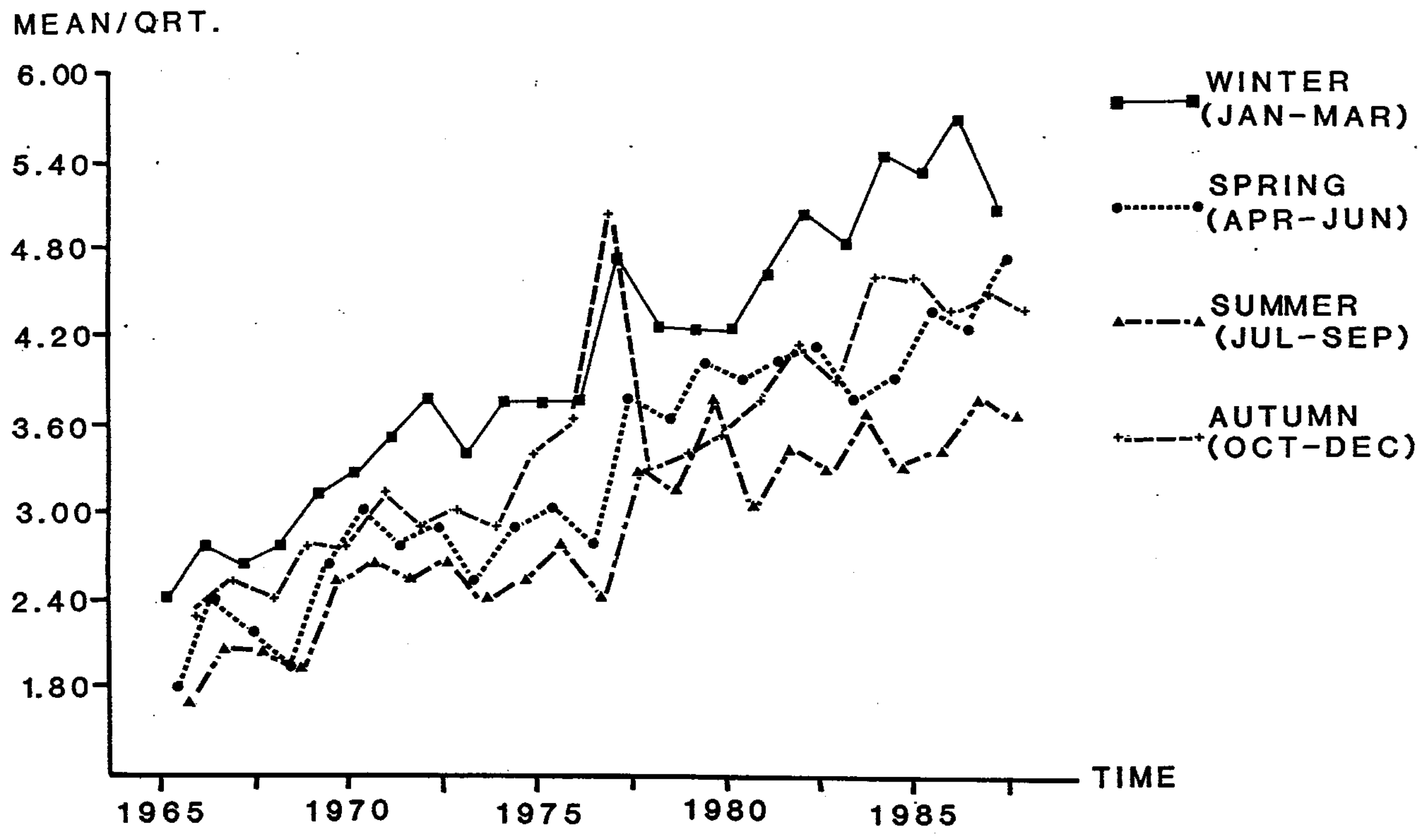


Figure 4.2 Changes in quarterly mean nitrate concentration (mg/l) based on weekly samples for the River Frome at East Stoke (Dorset) over the period 1965-87.

Table 4.3 Linear regression of weekly nitrate concentration (N) against year (T), separately for each season of the year. Data from River Frome at East Stoke 1965-87.
Regression equation : $N = a + b.T$; standard errors in brackets
r^2 = % total variation in weekly concentrations explained
r_T^2 = % of between year variation explained

Season	a	(SEa)	b	(SEb)	r_2	r_T^2
JAN-MAR	2.49	(0.056)	0.135	(0.004)	77%	94%
APR-JUN	2.00	(0.053)	0.113	(0.004)	72%	89%
JUL-SEP	1.93	(0.056)	0.083	(0.004)	55%	84%
OCT-DEC	2.41	(0.074)	0.100	(0.006)	51%	75%

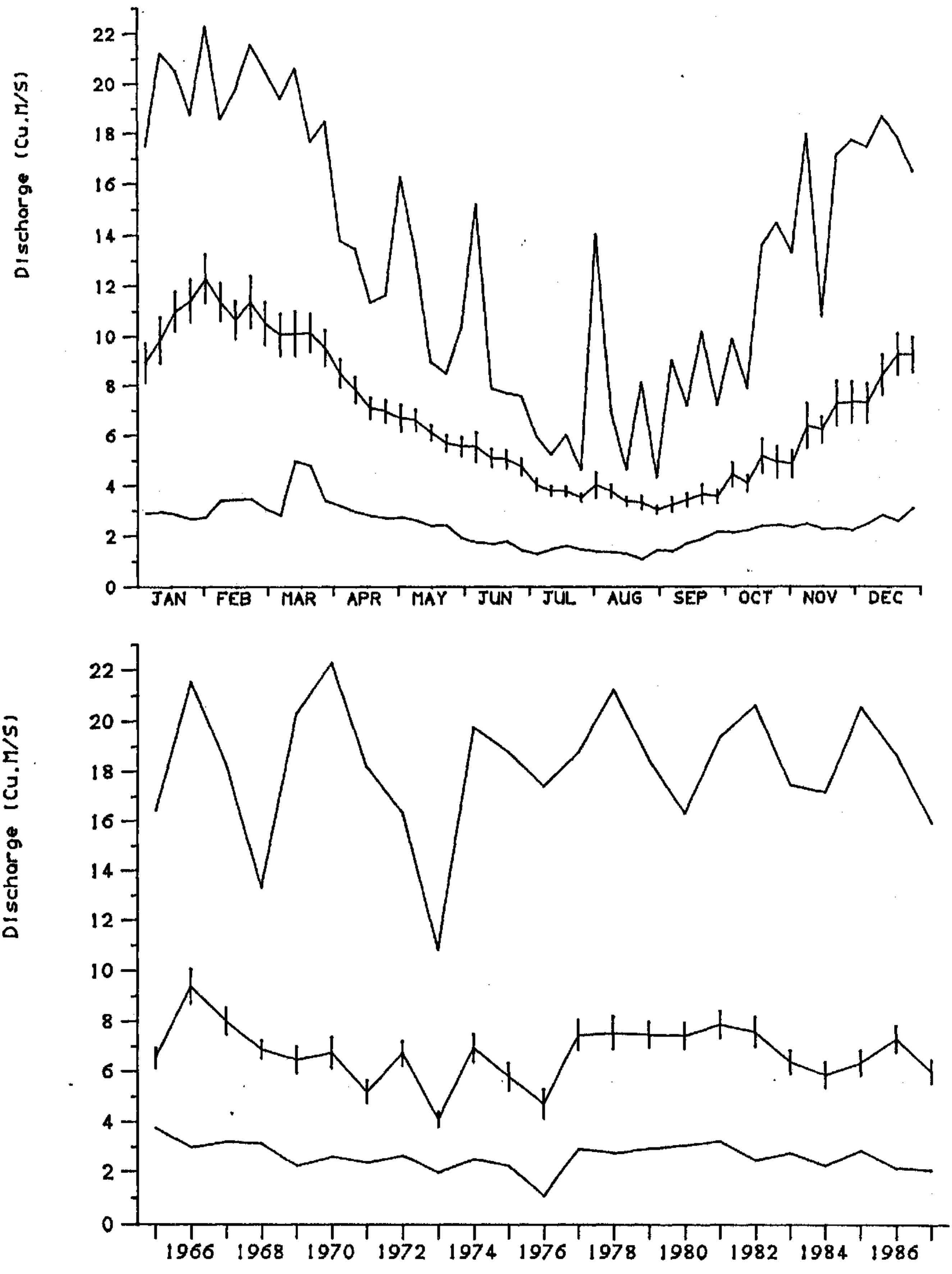
4.5 <u>Discharge regime over the period 1965-87</u>

The annual and seasonal variation in mean daily discharge at the sampling site over the 23 years is shown in Table 4.4 and figure 4.3. There has been no long-term change in discharge, which means any major increase in nitrate loading is due just to the increase in concentration. There is a cyclical seasonal pattern to the discharge, ranging from a average of 3 $m^3 s^{-1}$ in August to 12 $m^3 s^{-1}$ in January/Febuary.

Table 4.4 Annual statistics for daily mean discharge ($m^3 s^{-1}$) in the River Frome at East Stoke, Dorset.

Year	Mean	S.E.	Minimum	Maximum
1965	6.52	0.40	3.74	16.45
1966	9.38	0.68	2.98	21.54
1967	8.00	0.54	3.20	18.29
1968	6.87	0.37	3.12	13.29
1969	6.45	0.54	2.23	20.31
1970	6.75	0.63	2.60	22.28
1971	5.18	0.46	2.35	18.17
1972	6.73	0.49	2.65	16.34
1973	4.10	0.30	1.97	10.82
1974	6.94	0.56	2.51	19.75
1975	5.78	0.55	2.22	18.76
1976	4.70	0.59	1.07	17.41
1977	7.47	0.60	2.92	18.76
1978	7.54	0.67	2.74	21.24
1979	7.46	0.53	2.94	18.45
1980	7.41	0.52	3.06	16.30
1981	7.87	0.54	3.22	19.38
1982	7.57	0.61	2.44	20.60
1983	6.36	0.47	2.74	17.44
1984	5.84	0.52	2.23	17.13
1985	6.32	0.50	2.85	20.52
1986	7.29	0.54	2.13	18.63
1987	5.98	0.47	2.04	15.91

Figure 4.3 (A) Seasonal and (B) Annual summary statistics for discharge ($m^3 s^{-1}$) in the River Frome at East Stoke (Dorset) over the period 1965-87. For each year, and each week (1-52) of the year, the mean, minimum and maximum values are shown. Vertical bars denote ±1 standard errors.



4.6 Long-term trend in Nitrate Loading

Given a weekly spot value of nitrate concentration and daily mean discharges it is possible to estimate weekly and annual throughputs/loadings of nitrate in several ways :

(1) Derive a model predicting nitrate concentration for a given daily mean discharge; and use this to estimate the nitrate concentration on each of the 6 intervening non-sampled days of each week. Nitrate loading can then be estimated separately for each day and summed.

(2) Linearly interpolate between weekly nitrate values to estimate the intervening days.

(3) Calculate the nitrate load on just the weekly sampled days, and treat this loading as applying for one week.

Though the methods give numerically different estimates of loadings, they are highly correlated and the practical results are very similar. Method (3) has the advantages of simplicity and that actual values of both concentration and discharge from the same day are used. It is the method used for examining loadings in this report.
The annual variation and long-term trend are summarised is Table 4.5 and Figure 4.4. Nitrate loads have approximately doubled since 1965, in parallel with the doubling of nitrate concentration.

Table 4.5 Annual statistics for nitrate loadings (tonnes/week) in the River Frome at East Stoke, Dorset.

Year	Mean	S.E.	Minimum	Maximum
1965	8.51	0.76	3.58	29.85
1966	13.98	1.13	3.42	40.79
1967	11.50	0.89	3.30	24.00
1968	10.23	0.78	3.28	25.00
1969	10.97	0.99	3.26	31.13
1970	12.44	1.20	3.55	35.30
1971	9.61	1.01	3.16	32.03
1972	12.92	1.16	3.72	33.90
1973	7.24	0.68	2.42	20.48
1974	13.74	1.27	3.19	40.13
1975	12.08	1.32	3.46	39.41
1976	11.89	1.93	1.10	53.07
1977	17.99	1.83	5.26	51.74
1978	16.94	1.69	4.40	46.09
1979	18.26	1.50	6.13	44.32
1980	17.21	1.45	5.53	40.72
1981	19.34	1.55	5.67	60.36
1982	19.50	1.83	4.29	51.20
1983	16.50	1.46	4.43	51.26
1984	16.68	1.94	3.18	59.11
1985	17.29	1.64	5.57	47.68
1986	20.70	2.00	5.08	66.21
1987	16.83	1.51	4.10	45.42

4.7 Changes in the Seasonal Pattern of Nitrate Loading

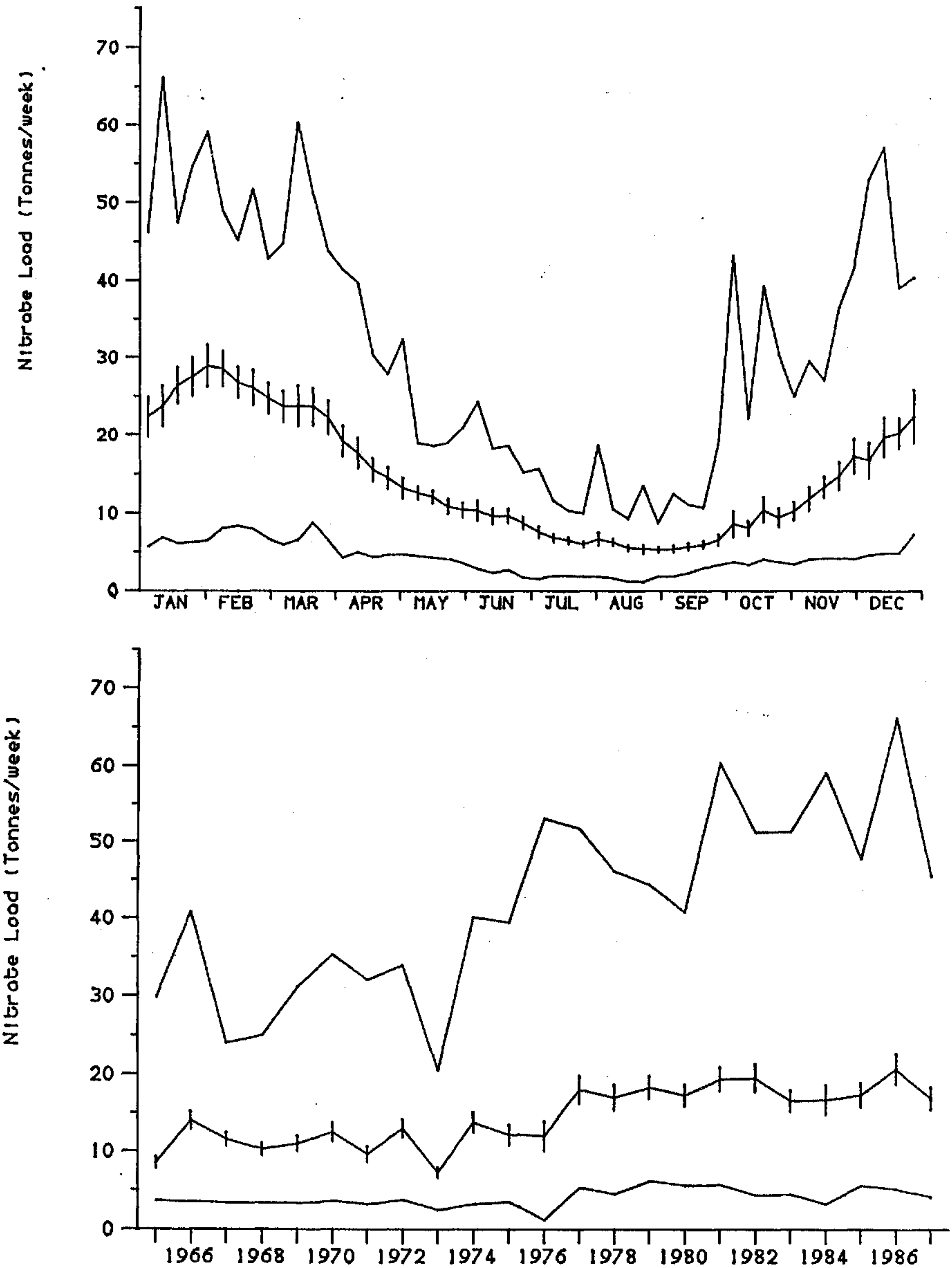
Both nitrate concentration and discharge have a seasonal cycle with highest levels in winter. Nitrate loadings, being the mathematical product of concentration and discharge, has a similar seasonal periodicity (Figure 4.4). However the nitrate loading is much more variable than the nitrate concentration (cf Figure 4.1), especially during the variable high winter flows. This graphically supports the conclusion of section 5 that in estimating loads rather than concentrations, the discharge variation is more influential, and needs to be sampled more frequently than nitrate concentration itself. Fortunately discharge values are usually more readily available from Water Authority gauging stations.

To see whether this seasonal pattern of nitrate loading has changed over the past 23 years, the estimated total quarterly loads for each year are shown in Table 4.6 and Figure 4.5.

Table 4.6 Total quarterly and annual nitrate loads (tonnes) in the River Frome at East Stoke (Dorset) over the period 1965-87.

Year	JAN-MAR	APR-JUN	JUL-SEP	OCT-DEC	Total
1965	156	79	62	146	443
1966	324	169	62	162	717
1967	248	124	59	169	600
1968	188	77	69	198	532
1969	282	122	68	99	571
1970	301	118	69	159	647
1971	257	114	56	68	495
1972	283	163	75	150	671
1973	183	87	47	57	374
1974	275	101	87	250	713
1975	327	129	69	100	625
1976	102	50	41	448	641
1977	482	215	89	141	927
1978	435	227	108	101	871
1979	377	279	124	161	941
1980	408	202	91	191	892
1981	380	268	118	239	1005
1982	465	192	77	282	1016
1983	379	214	100	161	854
1984	445	150	62	196	853
1985	432	199	97	166	894
1986	458	221	110	288	1077
1987	357	281	74	158	870

Figure 4.4 (A) Seasonal and (B) Annual summary statistics for nitrate load (tonnes/week) in the River Frome at East Stoke (Dorset) over the period 1965-87. For each year, and each week (1-52) of the year, the mean, minimum and maximum values are shown. Vertical bars denote ±1 standard errors.



Obviously the 1976 drought year was exceptional. The last of 1975/76 winter rains led to an unusually low winter nitrate load, followed by an exceptionally high autumn load with the first rains in autumn 1976. Table 4.7 shows linear regressions of the trend for each quarter's load excluding 1976. Because the loads are very variable and odd years might dominate the regression, a rank correlation test for long-term trend (including 1976) is also included.There are statistically significant increases in load over the period for every season except summer (July-Sept), where the inter-year variation may be masking the smaller increase.

Table 4.7 Linear regression of total nitrate load in tonnes N (L) against year (T) separately for each quarter/season of the year. Data from River Frome at East Stoke 1965-87.
Regression equation (Excluding 1976) : L = a + b.T
SE = Standard Error ; r^2 = % variation explained
r_s = Spearman Rank Correlation (including 1976)
P = Significance level of test that r_s=0

Season	a	(SEa)	b	(SEb)	r^2	r_s	P
JAN-MAR	217	(25)	11.0	(1.9)	62%	0.73	<0.001
APR-JUN	94	(18)	6.9	(1.4)	55%	0.69	<0.001
JUL-SEP	61	(7)	1.8	(0.6)	35%	0.59	<0.01
OCT-DEC	127	(23)	3.6	(1.8)	16%	0.34	>0.05

To remove the general trend in load and the between year variation, the quarterly total loads are expressed as percentages of the annual load in Table 4.8 and Figure 4.6. Linear regression and rank tests for trend did not reveal any statistically significant trends in the proportion of annual load being transported each season.
On average, 44% of the nitrates load is transported during the winter period January-March. In contrast, only 11% of the annual load is transported down the river during the summer period July-September.

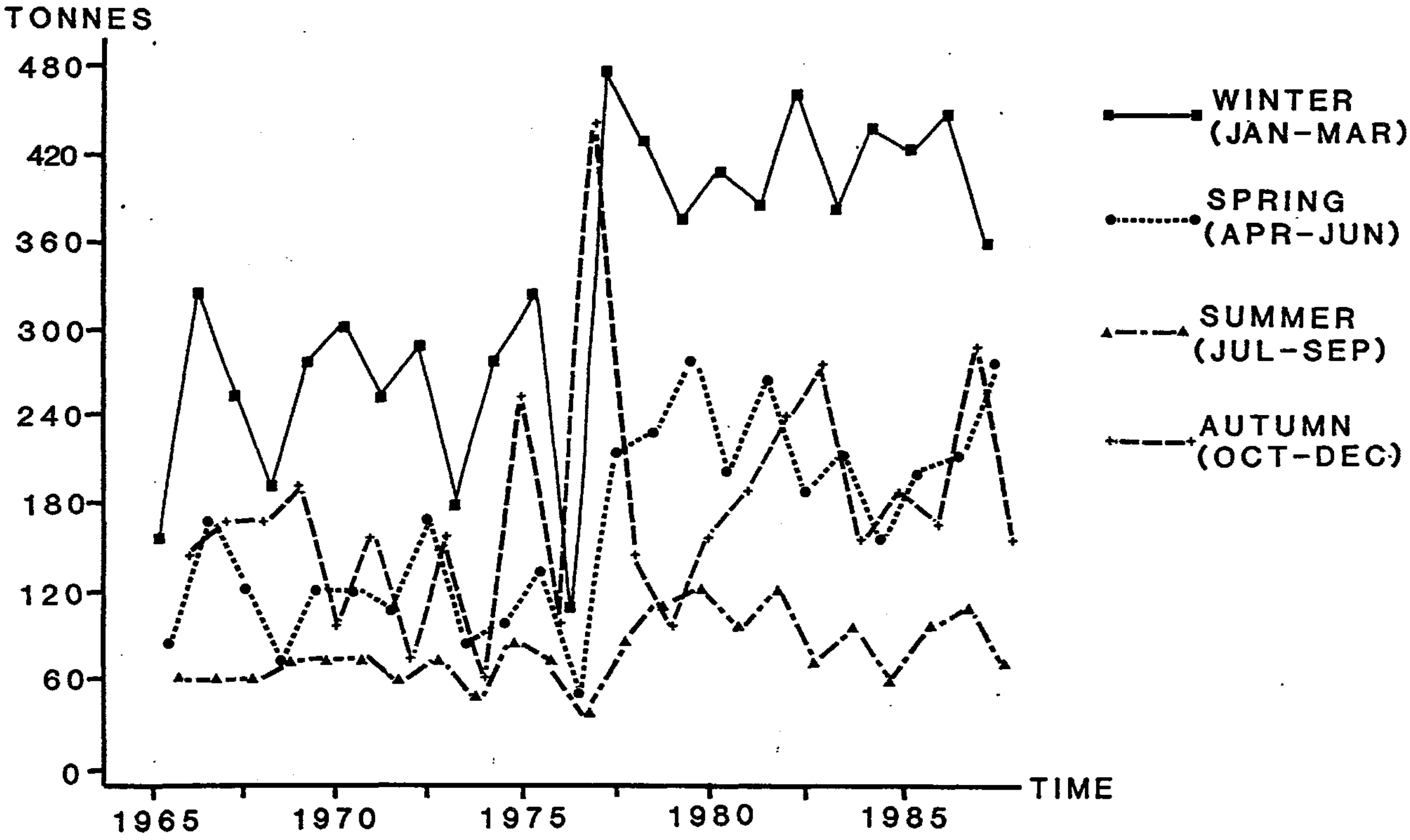


Figure 4.5 Changes in total quarterly nitrate load (tonnes) for the River Frome at East Stoke (Dorset) over the period 1965-87.

Table 4.8 Percentage of total annual nitrate load (tonnes) occurring in each season. Data from the River Frome at East Stoke (Dorset) over the period 1965-87.

Year	JAN-MAR	APR-JUN	JUL-SEP	OCT-DEC	Total Load
1965	35	18	14	33	443
1966	45	23	9	23	717
1967	41	21	10	28	600
1968	35	15	13	37	532
1969	50	21	12	17	571
1970	46	18	11	25	647
1971	52	23	11	14	495
1972	42	24	11	23	671
1973	49	24	13	15	374
1974	39	14	12	35	713
1975	52	21	11	16	625
1976	16	8	6	60	641
1977	52	23	10	15	927
1978	50	26	12	12	871
1979	40	30	13	17	941
1980	46	23	10	21	892
1981	38	26	12	24	1005
1982	46	19	7	28	1016
1983	44	25	12	19	854
1984	52	18	7	23	853
1985	48	22	11	19	894
1986	43	21	10	26	1077
1987	41	32	9	18	870
Average	44	21	11	24	

5 SAMPLING AND ERROR IN ESTIMATING NITRATE LOAD

In addition to simple monitoring the nitrate concentration levels in rivers, it is also of interest to know how much nitrate is being removed and transported down the river - termed the nitrate loading. Assume the nitrate load per day L (tonnes N / day) is to calculated as the product of the mean nitrate concentration for the day C (mg N/l) and the mean discharge Q (cumecs) by :

$$L = C * Q * k$$

where k=0.0864 is a units conversion constant.
Let the sample mean and standard deviation of concentration C over the period be denoted by u_c, s_c;
let the Coefficient of Variation of C = $CV_c = s_c / u_c$;
and similarly for Q and L.

Then the mean load is :

$$u_L = (u_c * u_Q + r_{cQ} * s_c * s_Q) * k$$

Notice that if the concentration is positively correlated with the day's flow, then the mean load is greater than the product of the mean concentration and mean flow; and vica versa.

The variance of the loads over the study periods is :

$$s_L^2 = ((u_Q s_c)^2 + (u_c s_Q)^2 + 2 r_{cQ} u_c u_Q s \ s) * k$$

Dividing by $(u_c u_Q k)^2$ gives :

$$s_L^2 = CV_c^2 + CV_Q^2 + 2 r_{cQ} CV_c CV_Q$$

Roughly speaking, this means that if the flows are twice as variable as the concentrations (i.e. have twice the CV) then they contribute four times as much to the variability in the loads. On the River Frome at East Stoke the average CV of nitrate concentration within a year (eliminating variation due to the long-term trend) is only 20% of the mean, whereas for flow it is 58%. Thus even in the River Frome, where flows are fairly stable, it initially appears that variation in flow causes over 80% of the variability in the nitrate load. This simple approach of assessing the relative contributions to variablility in load could be applied to any river.

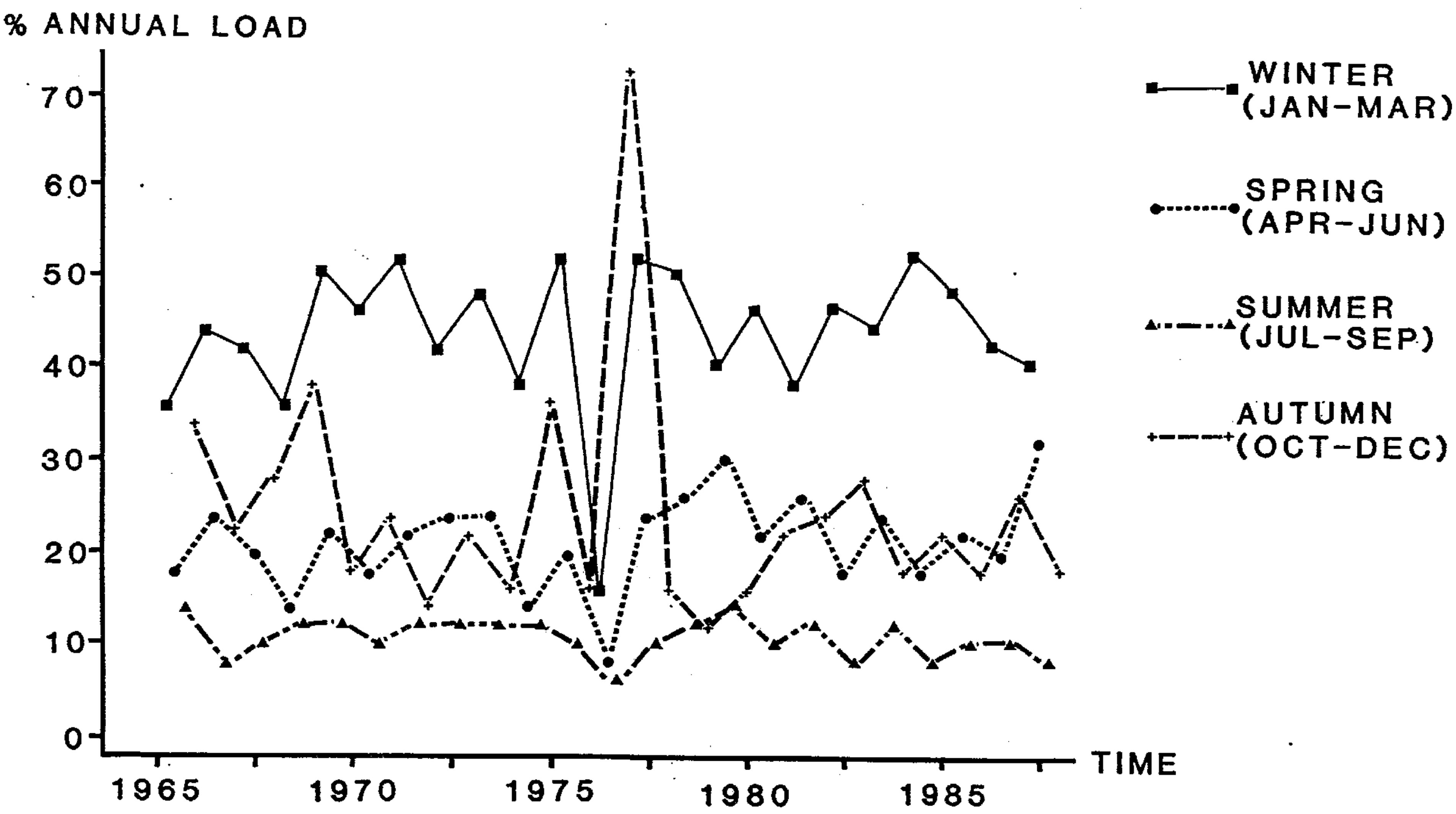


Figure 4.6 Percentage of total annual nitrate load occurring in each season for the River Frome at East Stoke (Dorset) over the years 1965-87.

6 TIME SERIES MODELLING OF NITRATES

The development of any time series models usually begins with computing the autocorrelations of a series of data.

If N(t) = Nitrate concentration at time t ;
where time may be in any units, such as 30 minute multiples, or weeks, then the autocorrelation of lag k, termed r(k), is defined as the correlation between values of N which are k time units apart.

i.e. r(k) = Correlation between N(t) and N(t+k)

6.1 Short-term autocorrelations in nitrate concentration

The nine months data of automated 30-minute nitrate sampling, described in section 3, was used to assess the extent to which current concentration is related to the previous few hours values. Though the sampling initially intended to obtain values every 30 minutes, the final record contained many 'missing' values. However it was still possible to calculate the autocorrelations from the available record of over 8000 values.
In order to only describe the real short-term relationship between successive nitrate values it was necessary to remove the seasonal 'deterministic' component of nitrate variation detected in the long-term record, as described in section 4. The 30 minute series of values was seasonally-adjusted by fitting a cosine wave peaking on day 35, which accounted for 64% of the total variance in nitrate values (Table 6.1). The resultant series was then used to compute the autocorrelations given in Table 6.2. The autocorrelations decay away very slowly and the first four partial autocorrelations, at least, are all significant.
Though a simple first-order autoregressive model on the seasonally-adjusted concentrations explains 87.5% of the total nitrate variation, and three extra autoregressive terms only explain a further 1.7% (Table 6.1), the first-order model is inadequate to use as a model to simulate the way nitrate changes behave. An adequate model of 30 minute behaviour would have to involve several complex terms and more frequent discharge data and is beyond the scope of this report.

From the residual standard deviations given in Table 6.1, we see that the very short term random variability in nitrate concentration has a standard deviation of just under 0.2 mg/l. This gives the absolute lowest limit of accuracy for any descripive or predictive model of nitrate concentration - at this site.

Table 6.1 Breakdown of variance of the nine month record of 30 minute sampling of nitrate concentration (mg/l).

Components Included	% variance explained	Residual Standard Deviation
NONE	0.0	0.538
Seasonal	64.5	0.321
Seasonal + Lag(1)	87.5	0.190
Seasonal + Lags(1-4)	89.2	0.177

Table 6.2 Autocorrelations and Partial Autocorrelations of the Seasonally-adjusted nitrate concentrations sampled at 30 minute intervals.

Lag	Hours Between	Auto - Correlation	Partial Auto-Correlation
1	0.5	0.804	0.804
2	1.0	0.760	0.321
3	1.5	0.728	0.173
4	2.0	0.699	0.100
5	2.5	0.675	.
6	3.0	0.649	.
7	3.5	0.617	.
8	4.0	0.586	.
9	4.5	0.566	.
10	5.0	0.536	.
11	5.5	0.509	.
12	6.0	0.493	.

6.2 Modelling the Long-term records of Nitrates

At most sites being monitored for nitrates, the main additional data available is usually the daily mean discharge at that site or a nearby comparable site. For instance, at East Stoke on the River Frome, weekly nitrate samples and daily mean discharges are both available since 1966. We have therefore restricted our attention to developing models based on using just nitrate and discharge data. Time series modelling based on the standard Box and Jenkins autoregressive moving average type models (Box and Jenkins, 1970) have been used in conjunction with multiple regression models. In this section we have looked at nitrate concentration in isolation. In section 6.3, we have briefly modelled the daily discharge pattern, and in section 6.4 we have combined this information into a simple model for nitrates as a function of discharge.

Before examining the autocorrelation pattern in successive weekly nitrate concentrations, the deterministic long-term trend and increasing seasonal component, as given by equation 4.3 of section 4, were removed from the series of values to give what is termed a 'stationary' time series. This removed 72% of the total variation in nitrate values over the 22 years. The adjusted series represents the variation about the norm for that year and time of year. It is this variation which we now examine to see if successive weeks' deviations from the norm are related.

There were 15 (non-consecutive) missing values over the 22 years, usually at Christmas !. Most time-series methods and computer packages cannot cope with missing values, so these were estimated by equation 4.3, which led to estimates of zero in the stationary adjusted series. Such a low proportion of missing values should not affect the analysis very much.

Let ARMA(i,j) denote an autoregressive moving-average model with i autoregresssive terms and j moving-average terms
 - see Box and Jenkins (1970) for further details.

The autocorrelations and partial autocorrelations of the adjusted series are given in Table 6.3. The correlation between successive weeks deviations in concentration is +0.403 , which is statistically highly significant ($P<0.001$), but not very high practically. Thus if one week's concentration is higher than average for the time of year, then there is some tendency for the next week's concentration to also be high, and vica versa. The first three partial autocorrelations are statistically significant, suggesting some dependence of current concentration on the previous three weeks concentrations. However, as shown in Table 6.4, these is little practical improvement in using any univariate model other than the simple ARMA(1,0) model :

$$N'_t = 0.403\ N'_{t-1} \qquad \text{(Eq 6.1)}$$

where N'_t = Adjusted nitrate concentration at time t.

Table 6.3 Autocorrelations and Partial Autocorrelations of the adjusted stationary nitrate concentrations sampled at weekly intervals in the River Frome (Dorset) between 1966-1987.

Lag (Weeks)	Auto - Correlation	Partial Auto-Correlation
1	0.403	0.403
2	0.276	0.136
3	0.267	0.141
4	0.214	0.056
5	0.171	0.031
6	0.198	0.086
7	0.152	0.009
8	0.108	-0.011
9	0.129	0.041
10	0.091	-0.014
11	0.094	0.026
12	0.062	-0.026

Table 6.4 Breakdown of total variance in nitrate concentration (mg/l) sampled weekly in the River Frome at East Stoke (Dorset) over the period 1966-87.

Components Included	% variance explained	Residual Standard Deviation
NONE	0.0	0.969
Trend	48.9	0.693
Trend + Seasonal	70.6	0.526
Deterministic = Trend + Increasing Seasonal	72.1	0.513
Deterministic + ARMA(1,0)	76.6	0.469
Deterministic + ARMA(1,1)	77.5	0.459
Deterministic + ARMA(3,0)	77.4	0.460

6.3 Times-series Analysis of Discharge

In section 4.5, it was shown that there has been no long-term change in discharge locally, but that there is a pronounced seasonal cycle (Figure 4.3). Because of the greater variability in discharges and the occasional very (relatively) high flows, discharge values are best analysed on a logarithmic scale (base e is used throughout). The seasonal component in daily mean discharge is well represented by a cosine wave peaking in late February (ie. after week 7 or day 49) :

$$\text{Log}_e \text{ Discharge} = 1.734 + 0.584 \text{ Cos(Day-49)} \qquad \text{(Eq 6.2)}$$

where Day=1,...,365

This removes 50% of the variation in daily mean discharge.
The autocorrelations and partial autocorrelations of the seasonally-adjusted discharges are given in Table 6.5.

Table 6.5 Autocorrelations and Partial Autocorrelations of the seasonally-adjusted $\log_e$ daily mean discharges ($m^3 s^{-1}$) for the River Frome (Dorset) between 1966-1987.

Lag (Days)	Auto - Correlation 1966-87	Partial Auto- Correlation 1966-87	1966-76	1976-87
1	0.950	0.950	0.960	0.925
2	0.893	-0.093	-0.086	-0.102
3	0.858	0.203	0.207	0.188
--	-----	------	------	------
4	0.831	0.022	0.033	0.005
5	0.805	0.046	0.037	0.048
6	0.780	0.019	0.002	0.034
7	0.760	0.047	0.056	0.031
8	0.741	0.009	0.001	0.013
9	0.725	0.049	0.059	0.033
10	0.711	0.016	0.028	0.000
11	0.699	0.049	0.037	0.058
12	0.690	0.028	0.007	0.047

The first three partial autocorrelations are all significant ($P<0.001$) and suggested the following ARMA(3,0) model :

$$D_t = a_1.D_{t-1} + a_2.D_{t-2} + a_3.D_{t-3}$$

This model was first fitted to all the 22 years data, then completely separately for each of the first and second 11 years of the period.

The precise dependence of current mean daily discharge on the three previous days' discharge appears not to have changed over the two decades (Table 6.6). The model estimated for the discharges in 1966-76 describes the discharges in 1977-87 as well as the model fitted specifically to the discharges in 1977-87; and vica versa. Despite the higher degree of variablility in discharge in the first 11 years (partly due to the 1975/76 drought), as measured by the Total SD, both periods are predictable to about the same degree of accuracy (residual SD = 0.126 for 1966-76 and 0.122 for 1977-86; Table 6.6).

Table 6.6 Consistency of an autoregressive model for seasonally-adjusted daily mean discharge ($m^3 s^{-1}$) for the River Frome at East Stoke over the period 1966-1987. SD = Standard Deviation

		Years used in model estimation		
		1966-87	1966-76	1977-87
	a_1	1.058	1.066	1.045
	a_2	-0.305	-0.308	-0.301
	a_3	0.204	0.210	0.191
	Total SD	0.409	0.468	0.330
Residual SD based on model estimated from years :	1966-76		0.126	0.122
	1977-87		0.127	0.122

6.4 <u>Modelling the relationship between nitrates and discharge</u>

In section 6.1 we saw how the de-trended seasonally-adjusted nitrate concentration in one week was positively correlated with the previous weeks' value. However this model can only predict a nitrate value knowing the previous week's value. It can be more useful to have an equation predicting nitrates from just deterministic components and discharges which are often more readily available.
In section 6.2 we saw how the daily mean discharge was to related the three previous days' discharge.

To use this information we have tried numerous models involving present and past discharges. One of the best simple regression models was an extension of model equation 4.3 in section 4.3, namely :

$$N = \underset{(0.029)}{2.212} + \underset{(0.002)}{0.109}\,YR + (\underset{(0.042)}{0.321} + \underset{(0.003)}{0.028}\,YR).CW + \underset{(0.094)}{1.134}\,SDWEEK - \underset{(0.090)}{0.798}\,SDDAY$$

with standard errors of coefficients in brackets (Eq 6.3)
and where SDDAY and SDWEEK are the seasonally-adjusted log discharges (using equation 6.2) for the current day, and averaged over the past week, respectively.

This and other models suggest that though nitrate concentration tends to be higher if current discharge is higher than average for the season; if the discharge has already been higher than average for several days (eg. the past week), then the higher the current day's flow the greater the chances of dilution effects through temporary exhaustion of nitrate supply within the catchment and groundwater system.

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8 ACKNOWLEDGEMENTS

The authors wish to thank Wessex Water Authority for providing recent discharge data, and the Surface Water Archive managed by the Institute of Hydrology for computer access to past daily mean discharges for the River Frome at East Stoke.

The Freshwater Biological Association is part of the Terrestrial and Freshwater Sciences Directorate of the Natural Environment Research Council.