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ANALYSIS OF WATER CHEMISTRY DATA FOR 28 RIVERS IN ATLANTIC CANADA

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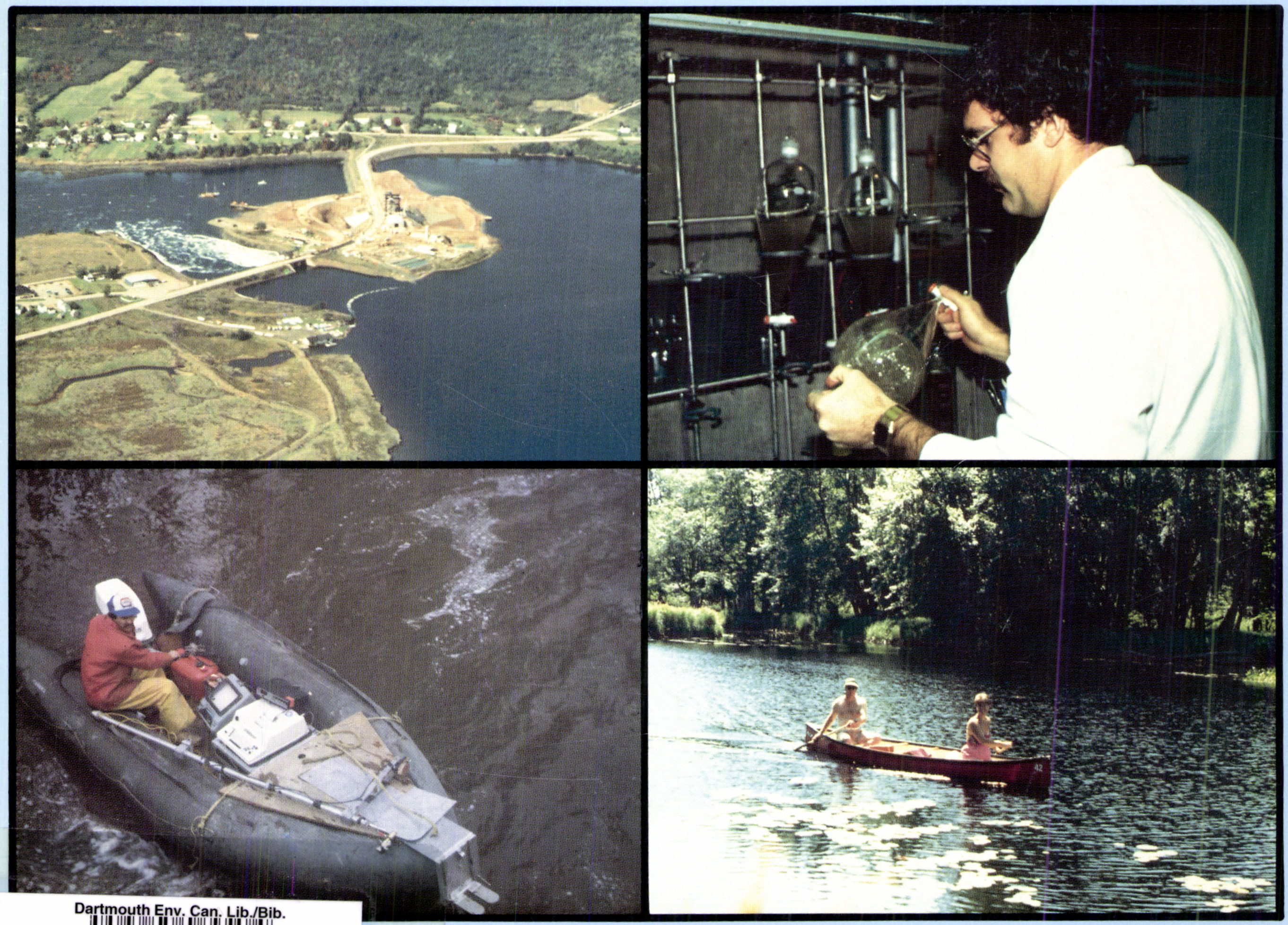

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

Canada

Analysis of Water Chemistry Data for 28 Rivers in Atlantic Canada

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4. Summary

The analyses described in this report were carried out in an effort to identify long term trends in water chemistry for 28 rivers in Atlantic Canada. We found that median levels of most chemical constituents, including pH and sulfate, have remained fairly constant over the approximately 20 year period of record for the rivers studied. However, levels of dissolved organic carbon and the variability of sulphate appear to have decreased since 1975. Due to the nature of the data, the statistical methods used were mainly exploratory and graphical.

5. Introduction

In recent years, there has been much concern over the potential or realized environmental impacts of the long-range transport of acidifying substances in the atmosphere (LRTAP). The Atlantic Provinces are a region of Canada where there is concern over the acidification of surface waters since: i) many surface waters are already acidic, possibly as a result of LRTAP (Shaw 1979; Watt et al. 1979; Thompson et al. 1980; Clair and Whitfield 1983); and ii) populations of Atlantic Salmon have disappeared from some acidic rivers, especially in southwestern Nova Scotia (Farmer et al. 1980; Watt et al. 1983).

Several studies done in Atlantic Canada have reported changes in water chemistry in recent decades. Watt et al. (1979) and Ogden (1980) resampled lakes near Halifax, Nova Scotia that had water chemistry data from 1955 (Gorham 1957). These authors reported consistent decreases in pH over that time period. Approximately 55% of the lakes had pH >5.5 and 7% had pH <4.5 in 1955, compared with 29% and 27%, respectively, in 1977. These decreases in pH (i.e. increases in acidity) occurred in virtually all lakes, on all bedrock types, and were largest in magnitude in lakes that were circumneutral in 1955. However, these data are limited in their usefulness because they are based on very limited samplings, and thus there is no information on the role of short-term temporal variations in pH. There were only single samplings of the lake waters in each of the study years, but they all occurred at about the same time of year.

In another study done in Nova Scotia, Watt et al. (1983) reported decreased pH of five rivers in the southwestern part of the province, by as much as almost a full pH unit. This study involved a comparison of pHs from the period 1954-55, to 1980-81. This study also reported decreases in alkalinity and sulfate in these rivers, and increases in dissolved aluminum (note however, that the sulfate comparisons in this study were invalid, since the earlier data were based on MTB-sulfate analyses, which systematically overestimate true concentrations in organically coloured waters (Kerekes 1983; see also below). To some extent, the study of Watt et al. (1983) suffered from the lack of a longer-term data base from which temporal changes could be assessed, and thus limited confidence can be placed on their assessment of acidification.

Thompson et al. (1980) reported time series of pH data for three rivers in Nova Scotia (data for 1955 and 1965 to 1973) and three in southern Newfoundland (data for 1971 to 1978). Their data showed a trend to sporadic decreases in discharge-weighted mean annual pH for the Nova Scotia rivers, but no evidence for change in the Newfoundland Rivers.

Finally, Clair and Whitfield (1983) reported a Box-Jenkins time series analysis of water quality data for seven rivers in Nova Scotia and four in Newfoundland. Their data records were fairly continuous, and extended as long as 1966-1974. Of the eight rivers that they characterized as being in watersheds that were sensitive to acidification on the basis of soil and bedrock geology, four showed evidence of decreasing pH, three did not change, and one could not be analyzed using their time series model. For calcium, three rivers showed evidence of a decrease in concentration, one increased, three did not change, and two did not fit the model. For sulfate, three rivers decreased, three increased, two did not change, and one did not fit the model.

The purpose of the present research report, is to present the results of a statistical analysis of water quality data for as many as 28 rivers in Atlantic Canada. For some of the rivers, data are available over 1966 to 1985, with sample sizes that exceed 200 dates over that period. The primary purpose of this analysis was to examine the data for longer-term temporal trends in water chemistry. The identification of shorter-term "events" of relatively high or low concentration was a secondary purpose.

6. Study Area

The data described and analyzed here are for 28 rivers in Atlantic Canada, with each having up to 18 water quality variables analyzed on each sampling date. For some rivers, the data extend over the years 1966 to 1985.

Locations of the rivers are described in Figure 1. Thirteen of the rivers are in Nova Scotia, 4 in New Brunswick, 2 in Prince Edward Island, and 9 in Newfoundland.

7. Source of Data

The data were obtained from the Inland Waters Directorate, Atlantic Region. The information had been gathered since 1966 as part of the routine water quality monitoring program of that agency. Because of the relatively long period of record for some of the watercourses, it was felt that it would be useful to perform a retrospective analysis of temporal patterns of concentration of chemical constituents that are of interest from the perspective of acidification of surface waters. However, it must be borne in mind that the data analyzed here were not originally collected for the purpose of such an analysis, and as a result they have important deficiencies that would not exist if a scientifically more appropriate sampling design had been used. These problems include irregular sampling intervals, long gaps in the data record for certain key variables, and inaccurate chemical analyses for one key chemical constituent in coloured waters (i.e. sulfate, see below).

For purposes of comparison to temporal patterns of chemical constituents, we also prepared analogue samples of monthly mean discharge for each watercourse. These data were retrieved from Water Resource Branch's hydrometric data base in Ottawa. Mean values were computed from hourly discharge measurements, and were then converted to a quantitative geometric/graphical presentation, separately for each month and year.

8. Chemical Analysis of Samples

The NAQUADAT codes (Anonymous 1984) for the various chemical analytical techniques that were used, are summarized below. Descriptions of the analytical techniques are in the NAQUADAT dictionary of parameter codes (Anonymous 1984):

a) Hydrogen Ion. NAQUADAT Code 10301.

b) Specific Conductance. NAQUADAT Code 02041.

c) Total Alkalinity. NAQUADAT Code 10101.

d) Gran Alkalinity. NAQUADAT Code 10110.

e) Turbidity. NAQUADAT Code 02073.

f) Dissolved Calcium. NAQUADAT Codes 20110, 20103, 20101, and 20102.

g) Dissolved Magnesium. NAQUADAT Codes 12102, 12104, and 12107.

h) Dissolved Potassium. NAQUADAT Codes 19102, 19103, and 19104.

i) Dissolved Sodium. NAQUADAT Codes 11102, 11103, and 11104.

j) Dissolved Chloride. NAQUADAT Codes 17205 and 17203.

k) MTB-Sulfate. NAQUADAT Codes 16303 and 16304.

l) IC-Sulfate. NAQUADAT Code16309.

m) Nitrate + Nitrite. NAQUADAT Codes 07308, 07110, 07105, and 07106.

n) Water Colour. NAQUADAT Code 02011.

o) Dissolved Organic Carbon. NAQUADAT Codes 06001, 06101, and 06107.

p) Dissolved Aluminum. NAQUADAT Codes 13101, 13303, and 13305.

q) Dissolved Iron NAQUADAT Codes 26304, 26102, and 26302.

r) Dissolved Manganese. NAQUADAT Codes 25304, 25101, 25304, and 25305.

For many of the chemical variables there were changes over time in the analytical techniques that were used (Appendix 22). In most cases, this was not of importance from the perspective of the present data analysis, since the various techniques were similarly accurate and precise. However, a notable exception is for sulfate. The earlier analyses were by the colourimetric methyl thymol blue (MTB) technique, which has been shown to seriously overestimate sulfate concentration in the organically coloured waters that are so frequent in Atlantic Canada (Kerekes et al. 1984). Since 1981, MTB-SO4 determinations have been supplanted by ion-specific ion chromatographic (IC) analysis, which has no colour interference. Since the MTB-sulfate determinations were continued even after the introduction of ion chromatography, there is a period of temporal overlap during which data were available for both analytical methods. Within our data set comprising 854 cases of analytical overlap among all of the watercourses, the MTB method yielded a mean (± S.D.) sulfate concentration of 4.2 ± 1.3 mg/L, while the IC method had 3.1 ± 1.4 mg/L. Note, however, that the discrepancies between the two methods of sulfate determination were much larger for the relatively brown waters. For example, in the Roseway River with mean colour of 107 Hazen units, the mean MTB-sulfate concentration was 4.6 ± 1.4 mg/L, compared with an IC-sulfate average of 2.3 ± 0.5 mg/L - a 100% difference (Table 1-13). Because the period of record for IC-sulfate is so short, we analyzed temporal patterns of MTB-sulfate. However, it must be borne in mind when interpreting the data for MTB-sulfate that it is a "composite" variable, i.e. its magnitude reflects variations in both sulfate and DOC-related water colour.

9. Clean-up of Data

The data files that were received from Inland Waters Directorate had already been subjected to scrutiny through their internal quality control programs. This included frequent analyses of blank samples to check for contamination, frequent analyses of duplicate and triplicate samples to check for precision, frequent analyses of standards to check for accuracy, and ion balance calculations.

Nevertheless, we also ran some quality control checks to further check for the occurrence of possible errors in either chemical analysis or data entry to the computer file.

The first data quality analysis involved calculations of ion balances (APHA 1976) for the data sets for each sampling date. Unfortunately, this technique had rather limited usefulness, especially for the pre-1981 data sets. The reasons for this were: i) many of the data sets had missing values for chemical variables that are important in ion balances. The case of DOC was already mentioned. Also important was magnesium; there were relatively few analyses for this constituent in the earlier data sets; and ii) the sulphate data for pre-1981 were obtained using the MTB technique, and were therefore erroneously high. In spite of this, the ion balances were frequently within acceptable limits; the reason for this is that the high MTB-sulphate values partially offset the fact that there were no estimates of organic anions for ion budget calculations covering this time period (there were few analyses of DOC, whic his required in the calculation of A^- by the method of Oliver et al (1983)).

Because the ion balances were of relatively little help to us, we decided to perform a simple statistical analysis that served to identify anomalous, outlier data points. This involved the following procedure: i) for each watercourse and each chemical constituent, we computed a 95% confidence interval comprised of ± 2 standard deviations of the mean; ii) we then used a computer program to flag all outlier data points that were beyond this confidence interval; and iii) the data set for the sampling date that included this data point was then inspected, and was eliminated from the data set if: 1) there was an obvious case of contamination by mineral acid used in the cleaning of sampling bottles, as indicated by very high values for nitrate, chloride, or sulfate accompanied by low pH values (note that such a case could still have an acceptable ion balance); or 2) there was an obvious case of order-of-magnitude error, which could have arisen from either an incorrect data entry, or an analytical problem. In case (2) we eliminated the particular datum, but not necessarily the entire data set for that date.

Overall, this was a fairly conservative approach and resulted in relatively few removals of data from the original file received from Inland Waters Directorate. Out of a total of more than 3000 individual records (i.e. sets of analyses for a particular watercourse on a particular date), only 21 were removed. Of these 16 were obviously contaminated by mineral acid from the bottle washing procedure; the others had order-of- magnitude problems with several individual constituents. Beyond this removal of data sets, some individual data points (i.e. analyses for particular constituents for a particular watercourse on a particular date) were also removed, because they differed from the overall average for their watercourse by approximately an order of magnitude. However, out of a total of more than 48,000 individual data points, only 91 were removed for this reason. The most common offender was nitrate, which accounted for 28 of the cases. Thus a very small fraction of the total data set was eliminated for these reasons. This reflects both the rather conservative approach used by us, and the high analytical quality of the data.

In addition, for some of the watercourses, there was a small number of duplicate or triplicate analyses of samples for particular dates, taken for quality control resons. In these cases, we retained the median values for each constituent among multiple analyses. Following this, there was only one data set for each sampling date.

Finally, seasalt-corrected values of sulphate were computed. These were based either on ratios of sulphate:chloride, or magnesium:chloride, and followed Watt et al (1979).

10. Chemical Characteristics of the Rivers

Tables 1-1 to 1-28 summarize the arithmetic mean values for each of the water quality variables of the various rivers. The rivers are briefly characterized below:

New Brunswick

River 1. Oromocto River. Data are available from 1969. This is a brownwater (64 Hazen units; DOC = 8.9 mg/L), circumneutral (pH 6.1) river.

River 2. Salmon River. Data are available from 1970. This is a brownwater (70 Hazen units; DOC = 9.4 mg/L), circumneutral (pH 6.5) river.

River 3. Lepreau River. Data are available from 1969. This is a slightly coloured (31 Hazen units; DOC = 5.4 mg/L), slightly acidic (pH 5.7) river.

River 4. Point Wolfe. Data are available from 1972. This is a clearwater (9 Hazen units; DOC = 3.2 mg/L), circumneutral (pH 6.7) river.

Prince Edward Island

River 5. Carruthers River. Data are available from 1966. This is a slightly coloured (32 Hazen units; DOC = 6.4 mg/L), neutral (pH 7.5) river. The wide range of values of conductivity, turbidity, and NO_x indicate a strong agricultural influence.

River 6. Dunk River. Data are available from 1966. This is a clearwater (9.6 Hazen units; DOC = 3.2 mg/L), neutral (pH 7.6) river. The wide range of values of conductivity, turbidity, and NO_x indicate a strong agricultural influence.

Nova Scotia

River 7. Medway River. Data are available from 1966. This is a moderately coloured (51 Hazen units; DOC = 7.9 mg/L), acidic (pH 5.4) river.

River 8. St. Mary's River. Data are available from 1966. This is a slightly coloured (25 Hazen units; DOC = 5.4 mg/L), slightly acidic (pH 6.0) river.

River 9. Meteghan River. Data are available from 1969. This is a brownwater (84 Hazen units; DOC = 9.5 mg/L), acidic (pH 5.6) river.

River 10. Avon River. Data are available from 1971. This is a moderately coloured (38 Hazen units; DOC = 5.5 mg/L), acidic (pH 5.4) river.

River 11. Kelley River. Data are available from 1970. This is a moderately coloured (49 Hazen units; DOC = 7.0 mg/L), slightly acidic (pH 5.8) river.

River 12. Tusket River. Data are available from 1966. This is a very brownwater (92 Hazen units; DOC = 11.9 mg/L), very acidic (pH 4.7) river.

River 13. Roseway River. Data are available from 1971. This is a very brownwater (107 Hazen units; DOC = 13.8 mg/L), very acidic (pH 4.5) river.

River 14. Rodger's Brook. Data are only available from 1983. This period of record is too short to consider with respect to annual trends, and hence this watercourse is not dealt with in detail.

River 15. Whiteburn Brook. Data are only available from 1983. This period of record is too short to consider with respect to annual trends, and hence this watercourse is not dealt with in detail.

River 16. Lehave River. Data are available from 1971. This is a moderately coloured (47 Hazen units; DOC = 7.1 mg/L), slightly acidic (pH 5.9) river.

River 17. Liscomb River. Data are available from 1971. This is a brownwater (72 Hazen units; DOC = 8.9 mg/L), acidic (pH 5.0) river.

River 18. Clam Harbour River. Data are available from 1969. This is a slightly coloured (28 Hazen units; DOC = 5.6 mg/L), circumneutral (pH 6.3) river.

River 19. Wallace River. Data are available from 1966. This is a clearwater (18 Hazen units; DOC = 4.6 mg/L), circumneutral (pH 6.7) river.

Newfoundland

River 20. Harry's River. Data are available from 1966. This is a moderately coloured (48 Hazen units; DOC = 6.5 mg/L), slightly acidic (pH 5.8) river.

River 21. Indian River. Data are available from 1971. This is a moderately coloured (41 Hazen units; DOC = 7.6 mg/L), circumneutral (pH 6.8) river.

River 22. Exploits River. Data are available from 1966. This is a slightly coloured (29 Hazen units; DOC = 8.1 mg/L), circumneutral (pH 6.5) river.

River 23. Grey River. Data are available from 1971. This is a moderately coloured (41 Hazen units; DOC = 5.7 mg/L), circumneutral (pH 6.0) river.

River 24. Grandy River. Data are only available from 1980. This period of record is too short to consider with respect to annual trends, and hence this watercourse is not dealt with in detail.

River 25. Isle Aux Morts River. Data are available from 1966. This is a moderately coloured (39 Hazen units; DOC = 5.3 mg/L), slightly acidic (pH 5.8) river.

River 26. Piper's Hole River. Data are available from 1966. This is a moderately coloured (36 Hazen units; DOC = 6.3 mg/L), circumneutral (pH 6.3) river.

River 27. Rocky River. Data are available from 1966. This is a brownwater (69 Hazen units; DOC = 9.2 mg/L), circumneutral (pH 6.2) river.

River 28. Garnish River. Data are available from 1971. This is a moderately coloured (47 Hazen units; DOC = 7.2 mg/L), circumneutral (pH 6.2) river.

11. Comparison of Rivers

The 28 rivers are compared with each other in Figure 2, using box and whisker plots (Tukey 1977) for selected chemical constituents. Briefly, the low end of the box indicates the 25th percentile or first quartile of the sample, the line through the box is the median, the upper end of the box is the 75th percentile or the first quartile, and the interquartile range (IQR) is the difference between the first and second quartiles. The "whisker" or line emanating from the box, indicates the range of the data within the quartiles plus or minus 1.5 times the IQR. The asterisks indicate outliers beyond these limits.

i) pH. The set of box plots for pH clearly show geographic affinities and differences among the rivers (Figure 2a). Rivers 1-4 are in New Brunswick, and are only slightly acidic. Rivers 5 and 6 from Prince Edward Island have almost identical medians, and relatively high pH. Rivers 7-19 are in Nova Scotia, and include the most acidic rivers in the data set, especially numbers 12, 13, and 17, which all have median pHs <5. Rivers 20- 28 are moderately acidic rivers in Newfoundland. Of these, numbers 23-28 are very similar in both median and range.

ii) Sulfate-MTB. The rivers differ relatively little in sulfate- MTB levels (Figure 2b), in spite of the great differences in acidity described above. The highest levels are for the least acidic rivers, numbers 5 and 6 in Prince Edward Island; the watersheds of these rivers have important agricultural land use and are chemically influenced by this source of nutrients. The Newfoundland rivers have a tendency to slightly lower sulfate-MTB levels than the other rivers. A general characteristic of the sulfate boxplots is the relatively large number of outlier values, most of which are high.

iii) Excess Sulfate-Cl. The overall pattern (Figure 2c) is rather similar to that of sulfate-MTB. There are few differences among the rivers, the highest levels are in the two Prince Edward Island rivers, and there are many high outlier values.

iv) Total Alkalinity. The pattern for alkalinity (Figure 2d) is an exaggerated inverse of that of pH. The two Prince Edward Island rivers have levels that are so much higher than those of the other rivers, that the scales of the latter are compressed, making comparison relatively difficult. Other than for P.E.I., rivers have median alkalinities less than 10 mg/L, and the more acidic rivers are <5 mg/L. Even for the relatively acidic rivers, there is a tendency for high, outlier values; these represent high-pH, high alkalinity events. Low-pH events are not represented by low-alkalinity outliers, since all samples with pH less than about 4.5 would have zero alkalinity.

v) Dissolved Organic Carbon. The rivers have a wide range in DOC, with little geographical pattern (Figure 2e). The two most acidic rivers (numbers 12 and 13 in Nova Scotia) have the highest values of DOC. Beyond this, there is no clear relationship between DOC and pH.

12. Statistical Analysis for Trends

12.1. Purpose of and General Approach to the Analysis.

The purpose of this analysis was to identify changes or trends over time in water quality variables that relate to acidification of surface waters. Our primary approach was to use statistical analysis as an exploratory tool, rather than for model-fitting. Thus, our statistical analysis was used to "listen" to the data, rather than to test hypotheses, or to confirm whether commonly used statistical models are useful descriptors of this sort of data. We felt that it was desirable to use this approach, since definitions of "change" or "trend" can be ambiguous. In addition, it was more important to see what the patterns were, rather than to test whether they agreed with preconceived notions of what they could be.

Patterns which we observed graphically were submitted to more detailed statistical modelling and testing. The purpose of these a posteriori models and tests was to compute statistical parameters which described the data, and to test whether there was evidence that the patterns could be due to random temporal variation.

12.2. Possible Statistical Models.

i) Box-Jenkins. Perhaps the most commonly used tool for time series analysis is the so-called Box-Jenkins method, which involves fitting an autoregressive moving average model to a time series. We chose not to use this technique because it is not well suited to the problem of quantification of trends and cycles. The series is usually either: 1) assumed to be stationary, with trends and cycles that are random and local and explained by autocorrelation; or 2) the series is differenced to achieve stationarity, in which case much of the information about trends and cycles is eliminated. Furthermore, the present observations are not evenly spaced and contain long periods of missing values. All of these factors make the identification and estimation of Box-Jenkins models difficult or impossible.

Before we decided against the use of Box-Jenkins or similar models, scatter plots were drawn in order to examine whether there were long periods of missing values. In addition, the frequency of sampling intervals was calculated for some rivers and variables. This revealed that sampling was not consistently regular; there were episodes of sporadic sampling for all rivers. For example, 65% of the pH measurements for the Medway River (No. 7) were made at sampling intervals of less than 28 days or more than 31 days, rather than the intended monthly interval. This river had a relatively good data record.

ii) Regression. Another approach to modelling time series data is to fit polynomial or harmonic time functions using conventional least squares techniques. For example, to determine whether there is a long-term data trend, one could fit a simple time function and test whether the slope is significantly different from zero. However, such a test can be misleading for at least two reasons: 1) it is rare that the trend is linear over time; for example a genuine change near the end of a time series may not be detected due to the preceding long time period during which it was relatively constant; and 2) the commonly used statistical tests for model parameters are known to be insensitive when there is autocorrelation in the time series, even if the model has been correctly specified.

12.3. Statistical Methods Used.

i) Scatter-plots. The first and most obvious procedure in this sort of time series analysis is to draw scatter-plots. These were done for all watercourses and chemical variables. These plots allowed an initial screening of the data to detect obvious anomalies, trends, events, or missing data records. These plots were also useful in detecting patterns in the data which may have been due to the method of chemical analysis.

ii) Running Boxplots. The purpose of this analysis was to investigate whether there were changes in the central location or dispersion of the data over time. This was done by calculating running medians and running 25th and 75th percentiles of the data for particular chemical variables for each watercourse. For a given record, the data were grouped by the 6 month periods before and after the date of the record. These data were then sorted and the 25th and 75th percentiles and median were calculated. This procedure was done for the entire period of record, and the statistics were displayed graphically by joining percentiles and medians by lines. In addition, the largest data-value within each one-year window was plotted as an asterisk. However, at the endpoints of the data record the window was either + 6 months for the beginning, or -6 months for the end. In some cases, this technique was used with a ±12 month window. This had the effect of smoothing the curves.

This box plot technique was useful in that it allowed us to study both the central trend and the dispersion of the data using the same graph. However, the algorithm for the endpoints is lacking in theoretical treatment. The best way to deal with this problem when examining the running box plots, is to pay less attention to results close to the endpoints.

iii) Median Plots. In some cases, annual medians were calculated and plotted. This was used as an exploratory tool for the detection of patterns, and as an aid to interpretation of some of the linear models.

iv) Linear Models. The results of the above analyses and the hypotheses generated by them were tied together by linear models. These models were essentially two-way ANOVA's of medians that were weighted according to the number of observations used in their calculation. The two factors used would be, for example, river and year. This procedure allowed us to estimate year effects after having accounted for effects due to rivers.

In addition, several variations of these models were used. In one case, instead of considering all the rivers, the data were grouped into Nova Scotia and Newfoundland rivers. In another case, instead of using all years, "before" and "after" years (for a date where important changes appeared to have occurred) were grouped to test differences in medians. The same types of models were used to study inter-quartile ranges, or their logarithms.

The parameters estimated from these models were useful in summarizing behaviour of the data over the entire period of record. This was important, since the primary purpose of our analysis was to determine whether water quality had changed over time. In the following, we describe the statistical procedure that was used:

Step 1. Yearly medians for each river and each water quality variable (medians were used instead of means because they are less influenced by extreme observations) were computed giving the the observation:

y_{ij}= annual median for river i in year j on one of the chemical variables.

In what follows, y_{ij} can stand for any of:

- square root of alkalinity;
- square root of dissolved organic carbon;
- pH (log base 10 of hydrogen ion); or
- square root of sulfate.

The decision to use square roots was based on preliminary analysis and examination of residuals for the original data. We found that the residual patterns were much more satisfactory after a square root transformation for alkalinity, dissolved organic carbon, and sulfate; pH showed reasonable residual behaviour without transformation.

Step 2. A two-way analysis of variance model was formulated as follows:

y_{ij}= mean + river$_i$ effect + year$_j$ effect + error.

This model was fitted using a two-way ANOVA where each median, y_{ij}, was weighted by the number of observations that contributed to its calculation. Thus, more weight is giver to those rivers and/or years with larger numbers of observations.

Step 3. We then determined whether there were significant year effects by testing:

H_o : y_{ij} = mean + river-effect $_i$ + error; and

H_1 : y_{ij} = mean + river-effect $_i$ + year-effect $_j$ + error.

The appropriate F-statistic was computed and the corresponding P- value determined. In this analysis, a small P-value indicates that there is a year-effect, while a large value of r^2 indicates a good fit of the model to the data. In addition, by examining the estimate of the year effect divided by the standard error, we determined which particular years had statistically significant effects. In this latter determination, a value of 2 for the t- statistic was used as the cutoff point.

This analysis was carried out for the Nova Scotia rivers (7, 11, 12, 13, 14, 16, 17, 18, 19) and the Newfoundland Rivers (20, 21, 22, 23, 25, 26, 27, 28). Rivers 8, 9, and 10 from Nova Scotia were eliminated from the analysis, as they occur on watersheds with calcareous material, and hence they are relatively non- susceptible to acidification. Rivers 15 and 24 had too short a period of record to analyze. In addition, the analyses for Nova Scotian and Newfoundland rivers were carried out on a seasonal basis, with summer being June to September, winter December to February, and spring March to May.

v) Before/After Medians. With some variables, the running boxplots indicated that median levels had changed substantially after a given year (in particular, DOC). To examine this phenomenon in greater detail, median levels before and after this year were calculated for each river.

vi) Hardware and Software. Initial data quality calculations were made using the CYBER computer of Dalhousie University. All other analyses were made using a VAX 785 operated by the Department of Mathematics, Statistics, and Computing Science. All of the graphics were done with the statistical package S provided by Bell Laboratories. Many of the simpler calculations and data management were also done with S. The running boxplots were plotted by S, but the calculations were done using FORTRAN programs which called statistical routines written by the Numerical Algorithms Group (NAG). Much of the data management was also done in this manner. The linear models were fit with GLIM (Generalized Linear Interactive Modelling) also written by NAG, and in some instances with S.

13. Results and Discussion

13.1. Scatter Plots.

The scatter plots are in Figures 3-7 and Appendices 1-9. Since there are almost 400 individual scatter plots, they will not all be commented upon. Rather, we will make general observations of common trends, and will discuss relatively outstanding features.

One important feature of the scatter plots is the gap of observations over approximately a five-year period in the middle of the data record for many of the rivers and chemical variables (for example, rivers 1, 6, 9, 10, etc.). Some rivers (for example river 3) did not have this gap, but data were relatively sparse within this period. In addition, the scatter plots for some rivers (14, 15, and 24) show that the their period of record was too short to be used to detect long-term trends.

Comments and discussion of the scatter plots for the various water quality variables are summarized below:

i) pH. Over the periods of record, the scatter plots do not show evidence for over-all trends to increases or decreases in pH of any of the watercourses (Figure 3). Each river varied in pH, frequently considerably, but the variation was symmetric and consistent around a stationary mean level. Thus, for none of the rivers, is there evidence from these data for changes in acidity over time.

There are clear patterns of periodicity for some of the rivers, for example rivers 9, 10, and 16. This probably reflects seasonality in hydrology, biological activity, or some other factor. We will not dwell on these patterns here; they are best examined using more intensive data records in conjunction with hydrologic data [see, for example Freedman et al. (1985) and Freedman and Clair

(1986) for such a treatment for four watercourses in southwestern Nova Scotia].

ii) Dissolved Organic Carbon (DOC). With one exception (river 22), data for DOC were only available for the most recent half of the study period (Figure 4). Thus, it is relatively difficult to assess longer-term trends. For some of the watercourses, there was a trend to decreases in mean values and in variation towards the end of the period of record. This is examined in more detail later, using running boxplots and before/after median analyses.

iii) Excess Sulfate (corrected using chloride ratios). A striking feature of this chemical variable for many of the rivers was a clear trend to decreasing variability towards the end of the period of record (especially rivers 3, 5, 6, 7, 8, 9, 11, 26, and 28) (Figure 5). However, there are no obvious longer-term changes in concentration of excess sulfate-Cl in any of the watercourses.

iv) Excess Sulfate (corrected using magnesium ratios). A decrease in variability is less apparent here, but can still be seen in rivers 5, 6, and 9 (Appendix 1). There are no obvious trends in concentration.

v) Sulfate-MTB. A decrease in variability over the period of record is especially apparent in rivers 5, 6, 8, 9, 11, 26, and 28 (Figure 6). Seasonal periodicity is evident, particularly for river 16. There are no obvious longer-term changes in concentration. Note that for some watercourses, there were runs of the same data value for varying periods of time (for example, around Julian day 3,000 for rivers 10, 20, 21, 22, 25, 26, 27, and 28). These runs are due to the numbers of significant figures reported for the chemical analyses; for other variables similar runs are due to concentrations being at or below the detection limit for the analytical method, so that values were assigned that were equal to the detection limit.

vi) Total Alkalinity. These data were extremely variable, and showed no obvious longer-term changes (Figure 7). For some watercourses, there were long runs of values at the detection limit. In some cases, the detection limit was lowered in recent years due to a change in analytical technique (for example, river 12).

vii) NO_x. These data were quite variable, with a pronounced tendency for sporadic outlier values for some of rivers (Appendix 2). Rivers having agriculture as an important land-use in their watersheds have relatively high mean concentrations of NOx, especially rivers 5 and 6 in Prince Edward Island. River 6 shows a weak trend to increasing mean levels in recent years.

viii) Calcium. Calcium levels appear to have remained stable over the period of record (Appendix 3).

ix) Iron. Iron levels appear to have remained stable over the period of record (Appendix 4). Rivers 21 and 25 have some extreme outliers, which may be related to episodes of iron-bearing turbidity.

x) Magnesium. Magnesium levels appear to have remained stable over the period of record (Appendix 5).

xi) Conductivity. Conductivity levels appear to have remained stable over the period of record (Appendix 6). There are tendencies to occassional extreme outlier values, for example rivers 1 and 12.

xii) Colour. Colour levels appear to have remained stable over the period of record (Appendix 7).

xiii) Turbidity. Turbidity levels appear to have remained stable over the period of record (Appendix 8). Many of the rivers have occassional, extreme outlier values, indicating episodes of high turbidity.

xiv) Sodium. Sodium levels appear to have remained stable over the period of record (Appendix 9). An exception is river 22, which has a pronounced increase in both mean and variance beginning around day 5000.

13.2. Running Boxplots.

The running boxplots are displayed in Figures 8-12 and Appendices 10-18. Again, because there are so many individual plots, they will not be commented on individually.

i) pH. The running boxplots for pH confirm the impression from the scatter plots which, generally speaking, is one of stability over time (Figure 8). Thus, there is no indication from these plots that pH has decreased over time; if anything there has been a slight increase. This slight increase is also seen in the before/after median studies.

ii) Dissolved Organic Carbon (DOC). Due to the short period of availability of data for DOC, it is difficult to infer much about longer-term changes (Figure 9). However, within this limitation there were some common patterns among the watercourses. Immediately before Julian day 6000 there was a pronounced decrease in DOC concentrations; this occurred in rivers 1, 2, 5, 6, 7, 8, 11, 19, 21, 22, 26, and 27. An opposite pattern occurred in rivers 9, 16, and 18. These changes in DOC are examined in more detail using before/after medians.

iii) Excess Sulfate (corrected using chloride ratios). There is no clear pattern of changes in median levels of excess sulfate-Cl over the period of record (Figure 10). The trend to reduced variability in recent years for some rivers is very clearly seen in their running boxplots, as indicated by decreased distance between the upper and lower running quartiles. This pattern is particularly evident in rivers 1, 5, 6, 7, 8, 11, 13, 18, 19, 21, 25, 26, and 27). The decrease in variability occurred around Julian day 3,000 for rivers 5, 6, and 8, and around day 4,000 for rivers 21, 22, 25, 26, 27, and 28).

Excess sulfate-Cl was also analyzed using running boxplots with a 12 month window, a treatment which gives a much smoother plot. With these plots, the recent decrease in variability also becomes apparent for rivers 3, 4, 6, and 9.

The change in variability is examined in more detail in Section C.

iv) Excess Sulfate (corrected using magnesium ratios). The patterns of these running boxplots are similar to those described above for excess sulfate-Cl (Appendix 10), although the variability and range of extreme outliers is less for excess sulfate-Mg.

v) Sulfate-MTB. The running boxplots for sulfate-MTB again indicate recent decreases in variability, particularly for rivers 5, 8, and 11 (Figure 11). However, the running boxplots for sulfate-MTB are considerably more erratic than for excess sulfate.

Sulfate-MTB was also examined using a ± 12 month window; with this smoothing treatment it is easier to see trends. This analysis shows a trend to long-term decreases in running median sulfate-MTB concentrations, for rivers 1, 3, 5, 6, 9, and 19. Rivers 13 and 17 show a slight long-term increase in concentration. The recent decreases in variability are also apparent in these plots.

vi) Total Alkalinity. The running boxplots do not show any obvious changes in total alkalinity in these rivers (Figure 12).

vii) NO_x. Increasing concentrations of NO_x are evident for rivers 5 and (especially) 6 in recent years (Appendix 11). The other watercourses do not show any obvious changes in NOx over the period of record.

viii) Calcium. Calcium levels appear to have remained stable over the period of record (Appendix 12).

ix) Iron. The patterns for iron are rather erratic (Appendix 13); the frequent outlier values have had a strong influence on the analysis. There are no clear patterns of change over the period of record.

x) Magnesium. Magnesium levels appear to have remained stable over the period of record (Appendix 14).

xi) Conductivity. Conductivity levels appear to have remained stable over the period of record (Appendix 15). Rivers 27 and 28 both show a large increase in conductivity around Julian day 4,000, with a return to baseline levels afterwards. This pattern is also seen weakly in rivers 11 and 20.

xii) Colour. Colour levels appear to have remained stable over the period of record (Appendix 16).

xiii) Turbidity. Turbidity levels appear to have remained stable over the period of record (Appendix 17). The occassional, extreme outliers have strong short-term effects for many rivers, but levels return to baseline after these episodes.

xiv) Sodium. Overall, most rivers have stable levels of sodium over the period of record (Appendix 18). However, certain watercourses have a tendency for sodium levels to meander (rivers 8, 9, 11, 12, and 18). The recent increases in conductivity in rivers 11, 20, 27, and 28 may be due to increases in their sodium levels; this pattern may reflect changes in road salting activity within their watersheds.

13.3. Year Effects.

Statistically significant year effects (t-values >2) are indicated in Table 2. This table summarizes the results of modelling using two-way ANOVA, designed to separate the total variation into river and year effects, separately for the groups of Nova Scotian and Newfoundland Rivers described in the Methods section. Note that all year effects are measured relative to year 1; the value of the year effect is given in the table, when significant. In addition, we have modelled year as a qualitative factor, which means that we obtain an estimated effect for each year. We used this approach, since fitting with a linear or quadratic term in year did not lead to models that fitted the data well (results of these models had lower r^2 values and more poorly behaved residuals than did the results of the two-way ANOVA presented here).

The results of this analysis are summarized below:

i) For all investigated variables, the analysis gave strong evidence for a year effect, and gave values of r^2 which indicate good to excellent fits of the models to the data. In total, all but 2 of the 30 analyses showed significant year effects at $p<0.05$.

ii) The effects for each variable were usually less pronounced for the seasonal than for the annual analysis, but the differences were not great.

iii) Nova Scotia alkalinity showed negative year effects in some of the later years, with one positive result in year 19 for winter. For Newfoundland, there were some negative effects in early and late years, and positive effects around year 10.

iv) There were few data for DOC in the early years. Nova Scotia had high values in years 10-15, and low values in years 16-20. Newfoundland had relatively high values over years 13-16.

v) pH results for Nova Scotia indicated relatively low values over years 5-8, and higher values in years 10, 13, and 19 (the latter based on yearly results). For Newfoundland, there were relatively low pHs over years 3-9.

vi) Nova Scotian sulfate values were frequently low relative to year 1, except in year 10. However, the overall pattern was one of stability. The interquartile range for sulfate was relatively large for several early and mid-years in Nova Scotia, and small for two later years. Newfoundland results were more mixed, but showed a trend to lower ranges in later years.

Since Table 2 does not give a complete summary of the results of this analysis (only significant observations are listed), we used the fitted year values from our ANOVA output and plotted these versus time for each of the variables considered (Figure 13). Note that the plotted year values within the Nova Scotia or Newfoundland sets of rivers, are corrected for river effect; however, the plots of fitted values for any particular river would have the same shape as in Figure 13, but would be shifted up or down by the amount of the river effect.

The following general conclusions can be drawn from the plots of fitted year values of variables versus time:

i) For both the median and interquartile range of sulfate there is a pronounced peak in 1975 for Nova Scotia, and in 1973 for Newfoundland. There is a general decrease in the interquartile range in the last 6-7 years of the record. For the median, Newfoundland shows a decline from 1980.

ii) For pH in Nova Scotia, years 1975 and 1978 were high. In Newfoundland, pH was low from about 1967 to 1974, and relatively high in other years except for 1983.

iii) Nova Scotia alkalinity shows relatively low values in 1979 and 1981, but an increase after 1981 to pre-1977 levels. The fitted values for Newfoundland peaked in 1975, but were generally erratic over time.

iv) Dissolved organic carbon values are based on a limited data set in terms of period of coverage. Nova Scotian values have declined somewhat since 1975, while Newfoundland values seem to have delined from a peak in 1980.

13.4. Before and After Medians.

This analysis compared the median for the years prior to year 15, with the median for year 15 and later. As noted earlier, after year 15 there appeared to be a large decrease in variability in the data in both scatter plots and running boxplots for water chemical variables. The results of this analysis are summarized in Table 3. Note that a value of 0 indicates that there were fewer than 5 observations, and the median was not calculated. The following patterns are evident:

i) Alkalinity. Alkalinity decreased in all eight of the Nova Scotian rivers, with the decrease being about 0.5 mg/L except in river 19 where it was about 2 mg/L. For Newfoundland, there were decreases in 5 of the 7 rivers, and a marginal increase in one of the other two.

ii) Dissolved Organic Carbon. For Nova Scotia, there was a fairly large decrease in DOC in the three rivers for which there were sufficient data to analyze. Similarly, in Newfoundland there were fairly large decreases in the four rivers for which there were sufficient data for analysis.

iii) pH. For Nova Scotia there was no consistent pattern of change, with increases in pH for four of the eight rivers, and a decrease in only one. For Newfoundland, there were small increases (about 0.2 pH unit) in all but one of the rivers.

iv) Sulfate. For Nova Scotia the changes were sporadic, with four increases and four decreases. For Newfoundland, there were decreases in five of the seven rivers.

13.5. Miscellaneous Topics.

The interpretation of the analyses presented here is out of necessity somewhat cursory. We have attempted to draw out the most striking patterns, in particular those for which we felt there was relatively strong statistical evidence, rather than attempt to explain every anomaly in every river. We stress that a more intensive interpretation of the data may reveal additional changes or patterns. This, however, would require further work and a more geochemical approach.

One topic which requires further investigation is that of seasonality. Two questions are of interest: i) what is the nature of the seasonal effect? This is best pursued using more intensive data sets than that examined here. Such data should be collected using a sampling design specifically suited to examining seasonal effects; and ii) have there been longer-term changes in seasonal behaviour of water quality variables? Preliminary analyses that we have done on the present data set indicate that these changes have not occurred.

Our analysis has paid little attention to variations of absolute or relative water flow. This is partly because of the enormous number of possible combinations of variables for calculations of correlations. In addition, many of the rivers have controlled flows, an important confounding factor. As noted above, we believe that more intensive data sets than the one used here, are better suited to the examination of the role of variations in water flow on concentrations of chemical constituents.

In addition, we have not investigated interrelationships among chemical variables. Such interrelationships do occur, but they can be difficult to substantiate using routine monitoring data such as are considered here. We feel that the best way to answer those particular questions is with data sets with more frequent sampling.

14. Conclusions

14.1. Directions for Future Collection of Data.

As noted previously, the data we have analyzed were not collected with the intention of doing this sort of analysis of temporal patterns. This has led to some difficulties of analysis and interpretation, because of irregular sampling intervals, long gaps in the data, missing data for key constituents from an acidification perspective, and inaccurate data for sulfate in coloured waters.

Given the potential ecological damages from acidic deposition from the atmosphere, it is of critical importance to collect, analyze, and interpret environmental data. However, improperly collected data may be of little use in the detection of relatively small changes in the environment, for example in acidity, alkalinity, dissolved organic carbon, or sulfate levels of surface waters. Inproperly collected data includes records that have sampling irregularities or gaps, critical missing variables, or inaccurate determinations of concentration. To greater or lesser degree, these were all problems with the data set that we examined here. As a consequence, only relatively large changes over time in the concentrations of chemical constituents would be detectable from analysis of the data. These comments underscore the need that better quality data be collected for future or ongoing analyses of temporal patterns in water quality, so that future changes can be more accurately assessed than past changes.

It is our feeling that, if resources are limited, it is best to concentrate such a collection of high quality data on a small number of "representative" rivers (the alternative is to gather poorer quality data on a larger number of rivers). The term "representative" is in quotes because it does not have a simple operational definition.

We also feel that the data analysis should be an ongoing process. The variability of chemical variables is due to both random and non-random factors. By analyzing data as it is collected, it is possible to design statistical tests which would identify non-random sources of variation as they occur. This would allow immediate action to be taken. For example, if there were sudden changes in hydrogen ion, sulfate or some other important constituent that were not explicable by seasonal, random, or other sources of variation, then data could be collected on potential causal factors such as weather patterns, changes in land use in the watershed, etc. Ten years after the event, it is difficult to identify explanations in a retrospective analysis. This suggestion takes its inspiration from the process of Statistical Process Control (SPC). SPC is used predominantly to determine when non-random factors (such as technological breakdown or change, manpower changes, etc.) are causing important or unacceptable effects on a manufacturing process. SPC methods can be used to monitor environmental variables as well, as we feel that a similar process should be applied in the case of LRTAP environmental research.

14.2. Conclusions from the Data Analysis.

In a capsule, we have found that:

i) Median levels of most chemical constituents, including pH and sulfate, have been fairly constant over time; and

ii) Levels of dissolved organic carbon, and variability of sulfate appear to have decreased since 1975.

15. References

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16. Tables, Figures, Appendices

Table 1 (1-28). Chemical characteristics, sample size, and period of record for each of the rivers.

Table 1-1

River: Oromocto, N. B.; River No. 1

Period of record: 146, 1969 to 130, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		12.5 ± 3.2	7.3 - 19.7
pH	114	6.1 ± 0.5	4.0 - 7.6
conductivity (uS)	114	29 ± 12	16 - 128
turbidity (JTU)	113	1.3 ± 1.5	0.1 - 13.0
colour (Hazen units)	114	64 ± 30	5.0 - 160
Na (mg/L)	114	2.0 ± 1.7	1.0 - 19.0
Mg (mg/L)	96	0.55 ± 0.13	0.35 - 0.90
K (mg/L)	114	0.35 ± 0.18	0.10 - 1.20
Ca (mg/L)	114	2.5 ± 0.7	1.2 - 5.1
Al (mg/L)	36	0.14 ± 0.07	0.02 - 0.33
Mn (mg/L)	69	0.026 ± 0.022	0.006 - 0.140
Fe (mg/L)	58	0.27 ± 0.13	0.02 - 0.57
Cl (mg/L)	114	2.8 ± 2.8	0.9 - 29.0
SO_4-MTB (mg/L)	114	4.6 ± 1.7	2.0 - 16.2
SO_4-IC (mg/L)	25	3.0 ± 0.9	1.0 - 5.5
NOx (mg/L)	89	0.055 ± 0.076	0.001 _ 0.370
DOC (mg/L)	33	8.9 ± 3.4	3.5 - 17.0
T-Alk (mg/L)	100	4.0 ± 2.1	1.0 - 11.5
G-Alk (mg/L)	17	2.1 ± 1.4	0.3 - 6.0

Table 1-2

River: Salmon, N. B.; River No. 2

Period of record: 307, 1970 to 063, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		24.6 ± 5.6	15.7 - 35.4
pH	93	6.5 ± 0.6	4.9 - 7.4
conductivity (uS)	94	44 ± 20	15 - 101
turbidity (JTU)	92	1.2 ± 0.9	0.1 - 3.8
colour (Hazen units)	89	70 ± 28	10 - 120
Na (mg/L)	93	2.8 ± 1.4	1.0 - 6.8
Mg (mg/L)	94	0.71 ± 0.29	0.25 - 1.60
K (mg/L)	92	0.38 ± 0.17	0.10 - 1.10
Ca (mg/L)	93	4.6 ± 2.4	1.0 - 11.0
Al (mg/L)	36	0.13 ± 0.07	0.01 - 0.27
Mn (mg/L)	60	0.043 ± 0.032	0.010 - 0.200
Fe (mg/L)	48	0.34 ± 0.13	0.02 - 0.64
Cl (mg/L)	94	2.2 ± 1.0	0.9 - 5.6
SO_4-MTB (mg/L)	94	6.6 ± 2.1	3.2 - 13.0
SO_4-IC (mg/L)	25	6.2 ± 2.4	2.8 - 10.8
NOx (mg/L)	70	0.075 ± 0.214	0.001 - 1.40
DOC (mg/L)	46	9.4 ± 4.7	3.2 - 24.6
T-Alk (mg/L)	86	10.0 ± 7.6	1.0 - 36.4
G-Alk (mg/L)	9	1.4 ± 1.4	-1.3 - 3.5

Table 1-3

River: Lepreau, N. B.; River No. 3

Period of record: 015, 1969 to 115, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		7.45 ± 1.56	4.57 - 12.0
pH	121	5.7 ± 0.5	4.6 - 7.3
conductivity (uS)	121	28 ± 9	20 - 91
turbidity (JTU)	121	0.82 ± 0.56	0.10 - 3.60
colour (Hazen units)	121	31 ± 16	5 - 100
Na (mg/L)	119	2.2 ± 0.7	1.3 - 7.3
Mg (mg/L)	102	0.42 ± 0.15	0.23 - 1.30
K (mg/L)	119	0.43 ± 0.25	0.10 - 2.80
Ca (mg/L)	120	1.7 ± 0.8	0.8 - 7.2
Al (mg/L)	32	0.21 ± 0.09	0.07 - 0.44
Mn (mg/L)	65	0.031 ± 0.028	0.010 - 0.160
Fe (mg/L)	55	0.20 ± 0.12	0.04 - 0.67
Cl (mg/L)	119	3.1 ± 1.7	1.8 - 15.0
SO_4-MTB (mg/L)	117	4.3 ± 0.9	2.0 - 7.6
SO_4-IC (mg/L)	16	3.5 ± 0.6	2.7 - 5.0
NOx (mg/L)	97	0.041 ± 0.047	0.001 - 0.250
DOC (mg/L)	41	5.4 ± 1.9	2.8 - 10.0
T-Alk (mg/L)	92	2.3 ± 1.7	0.5 - 10.5
G-Alk (mg/L)	38	0.52 ± 0.68	-1.47 - 1.60

Table 1-4

River: Point Wolfe, N. B.; River No. 4

Period of record: 196, 1972 to 067, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		5.37 ± 1.21	3.85 - 7.87
pH	82	6.7 ± 0.4	5.9 - 7.5
conductivity (uS)	82	37 ± 6	23 - 52
turbidity (JTU)	83	0.32 ± 0.41	0.10 - 3.40
colour (Hazen units)	82	9 ± 6	5 - 30
Na (mg/L)	82	2.2 ± 0.4	1.3 - 3.8
Mg (mg/L)	81	0.60 ± 0.09	0.39 - 0.90
K (mg/L)	81	0.30 ± 0.17	0.10 - 1.20
Ca (mg/L)	82	3.2 ± 0.6	1.9 - 4.4
Al (mg/L)	32	0.061 ± 0.037	0.010 - 0.160
Mn (mg/L)	50	0.011 ± 0.005	0.005 - 0.040
Fe (mg/L)	14	0.044 ± 0.030	0.001 - 0.100
Cl (mg/L)	82	3.1 ± 1.0	1.7 - 7.7
SO_4-MTB (mg/L)	82	4.1 ± 0.9	2.0 - 7.0
SO_4-IC (mg/L)	12	4.0 ± 0.8	2.5 - 5.3
NOx (mg/L)	61	0.43 ± 0.17	0.11 - 0.83
DOC (mg/L)	39	3.2 ± 1.4	1.0 - 6.3
T-Alk (mg/L)	79	5.3 ± 2.1	1.7 - 11.5
G-Alk (mg/L)	4	4.6 ± 2.0	1.9 - 6.7

Table 1-5

River: Carruthers, PEI; River No. 5

Period of record: 161, 1966 to 142, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		0.99 ± 0.19	0.57 - 1.36
pH	161	7.5 ± 0.5	5.9 - 8.4
conductivity (uS)	161	173 ± 56	43 - 268
turbidity (JTU)	161	2.7 ± 4.7	0.1 - 42.0
colour (Hazen units)	161	32 ± 27	5 - 120
Na (mg/L)	158	5.7 ± 1.5	2.0 - 13.0
Mg (mg/L)	109	6.7 ± 2.6	1.4 - 11.5
K (mg/L)	157	0.94 ± 0.52	0.30 - 5.00
Ca (mg/L)	159	19 ± 8	3.6 - 42
Al (mg/L)	33	0.076 ± 0.069	0.010 - 0.350
Mn (mg/L)	77	0.045 ± 0.039	0.010 - 0.280
Fe (mg/L)	67	0.20 ± 0.20	0.01 - 1.40
Cl (mg/L)	157	10.0 ± 3.3	3.8 - 33.0
SO_4-MTB (mg/L)	159	7.6 ± 3.2	3.0 - 22.8
SO_4-IC (mg/L)	13	5.4 ± 1.0	4.1 - 7.1
NOx (mg/L)	151	0.92 ± 0.55	0.005 - 3.4
DOC (mg/L)	59	6.4 ± 3.4	0.5 - 16.0
T-Alk (mg/L)	158	60.7 ± 25.7	10.7 - 111
G-Alk (mg/L)	---	---	---

Table 1-6

River: Dunk, PEI; River No. 6

Period of record: 223, 1966 to 142, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		2.65 ± 0.49	1.66 - 3.39
pH	140	7.6 ± 0.4	6.5 - 8.8
conductivity (uS)	141	180 ± 32	62 - 274
turbidity (JTU)	138	5.4 ± 8.5	0.10 - 48.0
colour (Hazen units)	135	9.6 ± 11.1	5.0 - 100
Na (mg/L)	141	5.6 ± 1.0	3.2 - 12.2
Mg (mg/L)	96	4.7 ± 1.2	1.3 - 8.5
K (mg/L)	138	1.2 ± 0.5	0.5 - 3.0
Ca (mg/L)	141	22.9 ± 7.4	4.7 - 76.0
Al (mg/L)	42	0.12 ± 0.12	0.03 - 0.52
Mn (mg/L)	85	0.044 ± 0.028	0.010 - 0.160
Fe (mg/L)	72	0.30 ± 0.40	0.001 - 2.90
Cl (mg/L)	142	9.6 ± 1.3	6.4 - 16.0
SO_4-MTB (mg/L)	140	7.6 ± 1.7	3.7 - 15.3
SO_4-IC (mg/L)	15	6.8 ± 1.6	4.9 - 11.0
NOx (mg/L)	125	1.7 ± 0.8	0.01 - 3.3
DOC (mg/L)	56	3.2 ± 3.2	0.5 - 15.0
T-Alk (mg/L)	141	59 ± 14	6.5 - 83
G-Alk (mg/L)	---	---	---

Table 1-7

River: Medway, N. S.; River No. 7

Period of record: 017, 1966 to 135, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		41.4 ± 7.9	21.7 - 57.8
pH	191	5.4 ± 0.4	4.0 - 6.9
conductivity (uS)	190	30 ± 5	13 - 53
turbidity (JTU)	191	0.75 ± 0.75	0.10 - 5.10
colour (Hazen units)	192	51 ± 21	5.0 - 100
Na (mg/L)	191	3.0 ± 0.5	1.1 - 5.8
Mg (mg/L)	141	0.53 ± 0.11	0.20 - 1.00
K (mg/L)	192	0.30 ± 0.15	0.10 - 1.20
Ca (mg/L)	193	1.1 ± 0.3	0.40 - 2.3
Al (mg/L)	57	0.13 ± 0.04	0.05 - 0.23
Mn (mg/L)	102	0.035 ± 0.025	0.010 - 0.240
Fe (mg/L)	91	0.21 ± 0.08	0.02 - 0.43
Cl (mg/L)	192	4.7 ± 0.9	1.8 - 10.4
SO_4-MTB (mg/L)	191	3.8 ± 1.1	1.0 - 9.0
SO_4-IC (mg/L)	26	2.7 ± 0.4	2.1 - 3.8
NOx (mg/L)	153	0.021 ± 0.038	0.001 - 0.34
DOC (mg/L)	71	7.9 ± 2.9	0.5 - 19.5
T-Alk (mg/L)	149	1.3 ± 0.9	0.5 - 8.1
G-Alk (mg/L)	52	0.40 ± 0.46	-0.33 - 1.80

Table 1-8

River: St. Mary's, N. S.; River No. 8

Period of record: 019, 1966 to 133, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		43.0 ± 7.3	28.2 - 58.0
pH	186	6.0 ± 0.4	3.8 - 7.2
conductivity (uS)	188	31 ± 9	20 - 99
turbidity (JTU)	189	1.1 ± 1.0	0.1 - 7.3
colour (Hazen units)	188	25 ± 13	5 - 80
Na (mg/L)	187	2.9 ± 0.5	1.9 - 4.7
Mg (mg/L)	123	0.63 ± 0.15	0.30 - 1.70
K (mg/L)	187	0.33 ± 0.16	0.10 - 1.30
Ca (mg/L)	189	1.4 ± 0.4	0.5 - 2.7
Al (mg/L)	39	0.082 ± 0.035	0.020 - 0.190
Mn (mg/L)	108	0.039 ± 0.024	0.006 - 0.160
Fe (mg/L)	94	0.17 ± 0.08	0.001 - 0.40
Cl (mg/L)	185	4.6 ± 0.8	2.6 - 7.5
SO_4-MTB (mg/L)	187	3.4 ± 1.1	1.6 - 9.0
SO_4-IC (mg/L)	11	2.3 ± 0.3	1.9 - 2.8
NOx (mg/L)	164	0.054 ± 0.094	0.001 - 0.61
DOC (mg/L)	60	5.4 ± 2.2	1.0 - 14.0
T-Alk (mg/L)	170	2.5 ± 1.5	0.5 - 12.6
G-Alk (mg/L)	19	1.5 ± 0.8	0.3 - 3.6

Table 1-9

River: Meteghan, N. S.; River No. 9

Period of record: 108, 1969 to 136, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		4.77 ± 1.04	3.12 - 6.65
pH	108	5.6 ± 0.3	4.5 - 6.2
conductivity (uS)	113	49 ± 7	29 - 77
turbidity (JTU)	113	0.87 ± 0.67	0.10 - 5.30
colour (Hazen units)	112	84 ± 21	40 - 140
Na (mg/L)	113	5.3 ± 0.6	2.6 - 6.8
Mg (mg/L)	95	0.97 ± 0.18	0.31 - 1.40
K (mg/L)	113	0.50 ± 0.24	0.20 - 1.70
Ca (mg/L)	113	1.8 ± 0.8	0.4 - 8.9
Al (mg/L)	38	0.17 ± 0.04	0.04 - 0.24
Mn (mg/L)	70	0.039 ± 0.015	0.006 - 0.070
Fe (mg/L)	59	0.33 ± 0.16	0.07 - 0.98
Cl (mg/L)	113	9.0 ± 1.4	3.7 - 12.2
SO_4-MTB (mg/L)	112	5.4 ± 1.2	3.8 - 10.9
SO_4-IC (mg/L)	27	3.3 ± 0.7	1.7 - 4.2
NOx (mg/L)	88	0.035 ± 0.029	0.001 - 0.14
DOC (mg/L)	34	9.5 ± 2.2	4.3 - 13.0
T-Alk (mg/L)	74	1.8 ± 2.0	0.5 - 17.6
G-Alk (mg/L)	48	1.1 ± 0.8	-1.7 - 2.6

Table 1-10

River: Avon, N. S.; River No. 10

Period of record: 106, 1971 to 107, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		-	-
pH	83	5.4 ± 0.3	4.6 - 6.2
conductivity (uS)	83	27 ± 4	18 - 40
turbidity (JTU)	85	0.92 ± 0.50	0.10 - 2.70
colour (Hazen units)	85	38 ± 15	5 - 80
Na (mg/L)	84	2.7 ± 0.4	1.8 - 3.7
Mg (mg/L)	84	0.43 ± 0.09	0.30 - 0.90
K (mg/L)	83	0.33 ± 0.13	0.10 - 0.80
Ca (mg/L)	84	1.0 ± 0.2	0.69 - 1.50
Al (mg/L)	34	0.20 ± 0.04	0.12 - 0.30
Mn (mg/L)	58	0.056 ± 0.020	0.005 - 0.110
Fe (mg/L)	48	0.24 ± 0.09	0.07 - 0.45
Cl (mg/L)	85	4.1 ± 0.8	2.5 - 5.9
SO_4-MTB (mg/L)	83	3.6 ± 0.8	2.4 - 7.9
SO_4-IC (mg/L)	15	2.9 ± 0.4	2.4 - 3.7
NOx (mg/L)	60	0.018 ± 0.017	0.001 - 0.080
DOC (mg/L)	29	5.5 ± 2.0	3.4 - 13.0
T-Alk (mg/L)	53	1.3 ± 0.7	0.5 - 4.2
G-Alk (mg/L)	44	0.35 ± 0.49	-1.0 - 1.6

Table 1-11

River: Kelley, N. S.; River No. 11

Period of record: 132, 1970 to 147, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		1.96 ± 0.31	1.56 - 2.61
pH	105	5.8 ± 0.6	4.2 - 7.7
conductivity (uS)	105	26 ± 6	17 - 54
turbidity (JTU)	105	0.69 ± 0.49	0.10 - 3.5
colour (Hazen units)	106	49 ± 25	5 - 100
Na (mg/L)	107	2.8 ± 0.9	1.1 - 6.0
Mg (mg/L)	104	0.51 ± 0.11	0.28 - 0.80
K (mg/L)	106	0.33 ± 0.18	0.10 ± 0.90
Ca (mg/L)	106	0.89 ± 0.26	0.42 - 2.40
Al (mg/L)	36	0.11 ± 0.04	0.03 - 0.20
Mn (mg/L)	87	0.049 ± 0.041	0.010 - 0.250
Fe (mg/L)	75	0.28 ± 0.14	0.001 - 0.67
Cl (mg/L)	105	3.4 ± 1.1	1.7 - 8.4
SO_4-MTB (mg/L)	106	3.4 ± 1.1	1.6 - 9.0
SO_4-IC (mg/L)	23	2.1 ± 0.5	1.0 - 3.3
NOx (mg/L)	82	0.035 ± 0.039	0.001 - 0.19
DOC (mg/L)	44	7.0 ± 3.4	2.0 - 17.4
T-Alk (mg/L)	83	2.8 ± 2.0	0.5 - 8.2
G-Alk (mg/L)	30	0.78 ± 1.08	-1.7 - 2.6

Table 1-12

River: Tusket, N. S.; River No. 12

Period of record: 019, 1966 to 136, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		32.8 ± 6.2	19.2 - 44.2
pH	158	4.7 ± 0.2	4.0 - 5.8
conductivity (uS)	160	40 ± 7	26 - 87
turbidity (JTU)	159	0.96 ± 0.92	0.1 - 7.0
colour (Hazen units)	159	92 ± 29	40 - 200
Na (mg/L)	161	3.9 ± 0.5	2.5 - 5.9
Mg (mg/L)	113	0.61 ± 0.12	0.4 - 1.1
K (mg/L)	159	0.33 ± 0.14	0.10 - 0.90
Ca (mg/L)	160	0.94 ± 0.28	0.40 - 2.0
Al (mg/L)	49	0.22 ± 0.08	0.010 - 0.37
Mn (mg/L)	92	0.019 ± 0.010	0.010 - 0.050
Fe (mg/L)	81	0.24 ± 0.11	0.001 - 0.45
Cl (mg/L)	161	6.3 ± 1.1	3.8 - 9.1
SO$_4$-MTB (mg/L)	160	4.6 ± 1.2	1.0 - 10.0
SO$_4$-IC (mg/L)	24	2.9 ± 0.4	2.3 - 3.6
NOx (mg/L)	112	0.019 ± 0.038	0.001 - 0.29
DOC (mg/L)	30	11.9 ± 3.9	4.0 - 21.0
T-Alk (mg/L)	107	1.0 ± 0.7	0.5 - 5.4
G-Alk (mg/L)	56	-0.84 ± 0.59	-2.05 - 0.63

Table 1-13

River: Roseway, N. S.; River No. 13

Period of record: 117, 1971 to 135, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		16.2 ± 3.0	9.28 - 22.8
pH	83	4.5 ± 0.2	4.1 - 5.3
conductivity (uS)	83	37 ± 6	25 - 55
turbidity (JTU)	82	0.62 ± 0.26	0.10 - 1.40
colour (Hazen units)	81	107 ± 25	40 - 200
Na (mg/L)	83	3.0 ± 0.4	2.3 - 4.3
Mg (mg/L)	83	0.45 ± 0.11	0.30 - 0.95
K (mg/L)	82	0.31 ± 0.13	0.10 - 0.90
Ca (mg/L)	83	0.58 ± 0.25	0.10 - 2.20
Al (mg/L)	34	0.23 ± 0.06	0.10 - 0.34
Mn (mg/L)	57	0.011 ± 0.005	0.010 - 0.030
Fe (mg/L)	46	0.19 ± 0.08	0.06 - 0.33
Cl (mg/L)	83	4.7 ± 0.8	3.3 - 7.5
SO_4-MTB (mg/L)	83	4.6 ± 1.4	1.6 - 10.0
SO_4-IC (mg/L)	25	2.3 ± 0.5	1.1 - 3.4
NOx (mg/L)	58	0.010 ± 0.007	0.001 - 0.030
DOC (mg/L)	32	13.8 ± 3.8	6.7 - 21.0
T-Alk (mg/L)	43	1.2 ± 1.2	0.5 - 7.2
G-Alk (mg/L)	51	-1.8 ± 0.9	-3.7 - 0.1

Table 1-14

River: Rodger's, N. S.; River No. 14

Period of record: 034, 1983 to 142, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		11.6	-
pH	288	5.2 ± 0.3	4.6 - 6.3
conductivity (uS)	289	36 ± 5	27 - 61
turbidity (JTU)	289	0.90 ± 0.59	0.40 - 5.10
colour (Hazen units)	288	84 ± 48	20 - 240
Na (mg/L)	288	3.6 ± 0.4	2.3 - 4.6
Mg (mg/L)	289	0.74 ± 0.17	0.39 - 1.40
K (mg/L)	287	0.27 ± 0.12	0.10 - 0.80
Ca (mg/L)	289	1.15 ± 0.30	0.20 - 2.20
Al (mg/L)	278	0.13 ± 0.05	0.01 - 0.31
Mn (mg/L)	287	0.041 ± 0.023	0.010 - 0.150
Fe (mg/L)	275	0.59 ± 0.50	0.15 - 2.90
Cl (mg/L)	286	5.4 ± 1.0	2.8 - 8.9
SO_4-MTB (mg/L)	288	4.7 ± 1.0	3.1 - 10.2
SO_4-IC (mg/L)	287	3.4 ± 0.9	1.3 - 8.1
NOx (mg/L)	288	0.017 ± 0.013	0.010 - 0.100
DOC (mg/L)	290	9.3 ± 5.1	3.4 - 38.0
T-Alk (mg/L)	1	3.1	-
G-Alk (mg/L)	288	0.52 ± 0.95	-3.1 - 3.6

Table 1-15

River: Whiteburn, N. S.; River No. 15

Period of record: 178, 1983 to 141, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		8.6	-
pH	12	5.8 ± 0.3	5.2 - 6.2
conductivity (uS)	12	36 ± 3	32 - 42
turbidity (JTU)	12	0.88 ± 0.48	0.30 - 2.10
colour (Hazen units)	12	47 ± 23	10 - 80
Na (mg/L)	12	4.1 ± 0.3	3.3 - 4.6
Mg (mg/L)	12	0.68 ± 0.11	0.55 - 0.90
K (mg/L)	12	0.36 ± 0.24	0.10 - 1.00
Ca (mg/L)	12	1.13 ± 0.18	0.85 - 1.40
Al (mg/L)	4	0.26 ± 0.22	0.13 - 0.58
Mn (mg/L)	12	0.058 ± 0.051	0.010 - 0.17
Fe (mg/L)	4	0.51 ± 0.16	0.33 - 0.68
Cl (mg/L)	12	6.2 ± 0.9	4.6 - 7.5
SO_4-MTB (mg/L)	12	3.0 ± 0.7	2.0 - 3.9
SO_4-IC (mg/L)	8	2.1 ± 1.0	1.0 - 3.8
NOx (mg/L)	12	0.029 ± 0.037	0.010 - 0.11
DOC (mg/L)	12	6.8 ± 1.5	5.1 - 9.6
T-Alk (mg/L)	3	2.5 ± 0.5	2.0 - 2.8
G-Alk (mg/L)	9	1.4 ± 0.9	0.3 - 3.1

Table 1-16

River: Lehave, N.S.; River No. 16

Period of record: 097, 1971 to 127, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		34.4 ± 7.1	17.6 - 49.8
pH	133	5.9 ± 0.3	4.8 - 6.6
conductivity (uS)	131	31 ± 5	20 - 51
turbidity (JTU)	115	0.64 ± 0.32	0.10 - 2.00
colour (Hazen units)	117	47 ± 15	10 - 80
Na (mg/L)	118	2.9 ± 0.4	2.0 - 4.4
Mg (mg/L)	123	0.63 ± 0.13	0.32 - 1.20
K (mg/L)	118	0.34 ± 0.12	0.10 - 0.70
Ca (mg/L)	123	1.52 ± 0.33	0.86 - 3.10
Al (mg/L)	61	0.15 ± 0.05	0.020 - 0.33
Mn (mg/L)	89	0.035 ± 0.013	0.010 - 0.080
Fe (mg/L)	81	0.21 ± 0.09	0.010 - 0.47
Cl (mg/L)	118	4.3 ± 0.8	2.1 - 6.8
SO_4-MTB (mg/L)	133	4.4 ± 1.4	2.0 - 12.5
SO_4-IC (mg/L)	32	3.3 ± 0.7	2.0 - 4.9
NOx (mg/L)	75	0.023 ± 0.022	0.001 - 0.10
DOC (mg/L)	43	7.1 ± 1.7	3.4 - 11.0
T-Alk (mg/L)	99	2.2 ± 1.2	0.5 - 5.5
G-Alk (mg/L)	46	1.1 ± 0.6	0.10 - 2.6

Table 1-17

River: Liscomb, N. S.; River No. 17

Period of record: 102, 1971 to 133, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		16.0 ± 3.0	10.7 - 23.3
pH	102	5.0 ± 0.3	4.1 - 5.9
conductivity (uS)	101	27 ± 6	16 - 72
turbidity (JTU)	99	0.78 ± 0.42	0.10 - 3.1
colour (Hazen units)	103	72 ± 25	20 - 160
Na (mg/L)	101	2.5 ± 0.8	1.6 - 8.9
Mg (mg/L)	100	0.42 ± 0.10	0.20 - 0.70
K (mg/L)	103	0.26 ± 0.19	0.10 - 1.1
Ca (mg/L)	102	0.81 ± 0.22	0.35 - 1.40
Al (mg/L)	39	0.16 ± 0.06	0.020 - 0.30
Mn (mg/L)	67	0.057 ± 0.017	0.010 - 0.090
Fe (mg/L)	54	0.34 ± 0.16	0.10 - 0.70
Cl (mg/L)	101	3.8 ± 1.5	1.9 - 16.5
SO_4-MTB (mg/L)	100	3.4 ± 1.0	1.5 - 7.0
SO_4-IC (mg/L)	25	2.2 ± 0.5	1.5 - 3.4
NOx (mg/L)	70	0.010 ± 0.008	0.001 - 0.040
DOC (mg/L)	35	8.9 ± 2.6	3.2 - 14.9
T-Alk (mg/L)	65	1.1 ± 0.9	0.5 - 5.5
G-Alk (mg/L)	53	-0.20 ± 0.48	-1.40 - 0.60

Table 1-18

River: Clam Harbour, N. S. ; River No. 18

Period of record: 105, 1969 to 128, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		1.65 ± 0.31	1.08 - 2.34
pH	108	6.3 ± 0.4	4.6 - 7.3
conductivity (uS)	112	40 ± 9	14 - 70
turbidity (JTU)	110	0.78 ± 0.79	0.10 - 5.2
colour (Hazen units)	111	28 ± 13	5 - 70
Na (mg/L)	111	3.4 ± 0.5	2.1 - 4.7
Mg (mg/L)	93	0.94 ± 0.28	0.50 - 1.8
K (mg/L)	110	0.29 ± 0.18	0.10 - 0.90
Ca (mg/L)	111	2.4 ± 0.9	1.3 - 6.1
Al (mg/L)	35	0.079 ± 0.047	0.017 - 0.25
Mn (mg/L)	68	0.034 ± 0.033	0.008 - 0.22
Fe (mg/L)	56	0.14 ± 0.07	0.050 - 0.31
Cl (mg/L)	112	5.5 ± 1.6	2.6 - 9.2
SO_4-MTB (mg/L)	110	4.3 ± 1.4	1.0 - 13.0
SO_4-IC (mg/L)	16	3.5 ± 0.9	2.2 - 5.9
NOx (mg/L)	84	0.037 ± 0.029	0.005 - 0.13
DOC (mg/L)	33	5.6 ± 1.7	2.8 - 9.1
T-Alk (mg/L)	101	4.7 ± 2.9	1.3 - 14.6
G-Alk (mg/L)	12	0.96 ± 1.28	-1.10 - 2.33

Table 1-19

River: Wallace, N. S.; River No. 19

Period of record: 148, 1966 to 113, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		8.89 ± 2.07	5.68 - 13.3
pH	122	6.7 ± 0.4	5.7 - 7.4
conductivity (uS)	120	48 ± 17	21 - 121
turbidity (JTU)	118	1.2 ± 1.3	0.1 - 8.9
colour (Hazen units)	117	18 ± 14	5 - 80
Na (mg/L)	120	4.3 ± 1.7	1.6 - 12.0
Mg (mg/L)	102	0.76 ± 0.17	0.25 - 1.2
K (mg/L)	118	0.40 ± 0.21	0.10 - 1.20
Ca (mg/L)	120	3.4 ± 1.2	1.6 - 9.0
Al (mg/L)	43	0.070 ± 0.051	0.010 - 0.27
Mn (mg/L)	77	0.020 ± 0.017	0.010 - 0.070
Fe (mg/L)	57	0.14 ± 0.08	0.040 - 0.36
Cl (mg/L)	117	6.4 ± 3.2	2.0 - 22.0
SO_4-MTB (mg/L)	120	3.9 ± 1.1	1.9 - 9.0
SO_4-IC (mg/L)	14	3.3 ± 0.9	2.2 - 5.7
NOx (mg/L)	107	0.062 ± 0.061	0.001 - 0.26
DOC (mg/L)	57	4.6 ± 2.7	1.3 - 13.0
T-Alk (mg/L)	118	7.8 ± 3.5	2.3 - 17.0
G-Alk (mg/L)	2	6.0 ± 2.8	4.0 - 7.9

Table 1-20

River: Harry's, NFLD; River No. 20

Period of record: 150, 1966 to 238, 1980

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		27.8 ± 2.7	24.5 - 32.0
pH	107	5.8 ± 0.4	4.5 - 7.3
conductivity (uS)	106	19 ± 4	11 - 45
turbidity (JTU)	105	0.84 ± 0.93	0.10 - 7.0
colour (Hazen units)	106	48 ± 16	20 - 100
Na (mg/L)	107	1.6 ± 0.4	0.9 - 5.1
Mg (mg/L)	86	0.48 ± 0.08	0.20 - 0.60
K (mg/L)	107	0.23 ± 0.16	0.10 - 1.4
Ca (mg/L)	108	1.0 ± 0.2	0.70 - 1.7
Al (mg/L)	1	0.090	-
Mn (mg/L)	35	0.029 ± 0.020	0.010 - 0.080
Fe (mg/L)	28	0.21 ± 0.13	0.001 - 0.63
Cl (mg/L)	107	2.6 ± 0.8	0.70 - 9.5
SO_4-MTB (mg/L)	106	2.4 ± 1.0	1.0 - 5.9
SO_4-IC (mg/L)	0	-	-
NOx (mg/L)	82	0.031 ± 0.032	0.001 - 0.22
DOC (mg/L)	1	6.5	-
T-Alk (mg/L)	105	2.3 ± 0.9	0.5 - 5.3
G-Alk (mg/L)	0	-	-

Table 1-21

River: Indian, NFLD; River No. 21

Period of record: 230, 1971 to 135, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		20.0 ± 2.9	15.4 - 25.5
pH	155	6.8 ± 0.4	4.2 - 7.8
conductivity (uS)	155	40 ± 8	23 - 63
turbidity (JTU)	153	1.2 ± 2.6	0.10 - 27
colour (Hazen units)	155	41 ± 16	5 - 90
Na (mg/L)	155	2.4 ± 0.5	1.3 - 4.5
Mg (mg/L)	155	1.3 ± 0.3	0.2 - 1.9
K (mg/L)	155	0.28 ± 0.17	0.10 - 1.4
Ca (mg/L)	156	3.3 ± 0.9	0.38 - 5.3
Al (mg/L)	44	0.12 ± 0.07	0.022 - 0.47
Mn (mg/L)	88	0.015 ± 0.011	0.005 - 0.080
Fe (mg/L)	66	0.24 ± 0.24	0.030 - 1.6
Cl (mg/L)	155	4.0 ± 1.0	2.1 - 7.9
SO_4-MTB (mg/L)	154	2.9 ± 1.1	1.6 - 7.8
SO_4-IC (mg/L)	19	1.4 ± 0.2	1.0 - 1.9
NOx (mg/L)	124	0.059 ± 0.039	0.001 - 0.18
DOC (mg/L)	56	7.6 ± 2.9	1.0 - 15
T-Alk (mg/L)	152	9.8 ± 3.2	0.50 - 19
G-Alk (mg/L)	2	0.25	-

Table 1-22

River: Exploits, NFLD; River No. 22

Period of record: 276, 1966 to 129, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		220 ± 28	165 - 275
pH	207	6.5 ± 0.4	5.0 - 8.2
conductivity (uS)	207	25 ± 4	10 - 44
turbidity (JTU)	206	0.89 ± 0.77	0.10 - 7.0
colour (Hazen units)	207	29 ± 11	5 - 90
Na (mg/L)	201	1.6 ± 0.4	0.4 - 4.6
Mg (mg/L)	150	0.47 ± 0.07	0.20 - 0.90
K (mg/L)	201	0.20 ± 0.10	0.10 - 0.70
Ca (mg/L)	208	2.4 ± 0.4	0.8 - 4.2
Al (mg/L)	45	0.084 ± 0.025	0.048 - 0.18
Mn (mg/L)	110	0.025 ± 0.017	0.010 - 0.11
Fe (mg/L)	92	0.13 ± 0.07	0.001 - 0.43
Cl (mg/L)	202	2.1 ± 0.4	1.1 - 5.1
SO_4-MTB (mg/L)	202	3.1 ± 1.1	1.3 - 9.4
SO_4-IC (mg/L)	17	2.6 ± 1.8	1.0 - 9.1
NOx (mg/L)	168	0.063 ± 0.059	0.001 - 0.61
DOC (mg/L)	53	8.1 ± 4.0	1.0 - 19.5
T-Alk (mg/L)	199	4.6 ± 1.4	0.5 - 11.2
G-Alk (mg/L)	5	3.7 ± 1.4	2.5 - 5.5

Table 1-23

River: Grey, NFLD; River No. 23

Period of record: 296, 1971 to 141, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		54.8 ± 14.0	23.4 - 66.8
pH	39	6.0 ± 0.5	5.2 - 7.3
conductivity (uS)	39	22 ± 9	10 - 47
turbidity (JTU)	38	0.64 ± 0.38	0.20 - 1.7
colour (Hazen units)	39	41 ± 25	5 - 100
Na (mg/L)	39	1.9 ± 0.7	0.9 - 4.6
Mg (mg/L)	38	0.36 ± 0.26	0.13 - 1.6
K (mg/L)	39	0.17 ± 0.09	0.10 - 0.40
Ca (mg/L)	39	1.3 ± 0.8	0.17 - 4.2
Al (mg/L)	11	0.14 ± 0.04	0.07 - 0.21
Mn (mg/L)	28	0.016 ± 0.010	0.010 - 0.060
Fe (mg/L)	16	0.21 ± 0.11	0.08 - 0.45
Cl (mg/L)	39	3.0 ± 1.4	1.4 - 8.0
SO_4-MTB (mg/L)	39	2.5 ± 0.8	1.5 - 5.0
SO_4-IC (mg/L)	8	1.3 ± 0.6	0.8 - 2.5
NOx (mg/L)	29	0.024 ± 0.023	0.005 - 0.090
DOC (mg/L)	15	5.7 ± 1.9	2.1 - 10.0
T-Alk (mg/L)	32	2.9 ± 2.5	0.5 - 13.6
G-Alk (mg/L)	10	0.89 ± 0.54	0.17 - 1.8

Table 1-24

River: Grandy, NFLD; River No. 24

Period of record: 312, 1980 to 141, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		17.7 ± 2.9	14.9 - 20.6
pH	19	5.9 ± 0.5	5.1 - 6.7
conductivity (uS)	19	18 ± 6	9.8 - 29
turbidity (JTU)	19	0.43 ± 0.21	0.20 - 1.1
colour (Hazen units)	19	30 ± 22	5 - 90
Na (mg/L)	19	1.6 ± 0.5	0.8 - 2.4
Mg (mg/L)	19	0.29 ± 0.11	0.10 - 0.54
K (mg/L)	19	0.17 ± 0.08	0.10 - 0.40
Ca (mg/L)	19	0.99 ± 0.50	0.14 - 2.1
Al (mg/L)	12	0.12 ± 0.05	0.062 - 0.20
Mn (mg/L)	19	0.011 ± 0.003	0.010 - 0.020
Fe (mg/L)	11	0.094 ± 0.028	0.050 - 0.15
Cl (mg/L)	19	2.3 ± 0.7	1.2 - 3.9
SO_4-MTB (mg/L)	19	2.2 ± 0.5	1.5 - 3.1
SO_4-IC (mg/L)	6	1.3 ± 0.3	0.8 - 1.8
NOx (mg/L)	12	0.046 ± 0.043	0.010 - 0.15
DOC (mg/L)	13	4.8 ± 1.9	2.2 - 8.6
T-Alk (mg/L)	10	2.4 ± 1.7	0.5 - 5.9
G-Alk (mg/L)	13	0.87 ± 0.63	-0.050 - 2.0

Table 1-25

River: Isle Aux Morts, NFLD; River No. 25

Period of record: 258, 1966 to 134, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		14.0 ± 1.6	10.7 - 16.4
pH	156	5.8 ± 0.5	4.4 - 7.0
conductivity (uS)	156	34 ± 14	14 - 91
turbidity (JTU)	153	0.66 ± 0.62	0.10 - 3.0
colour (Hazen units)	156	39 ± 22	5 - 100
Na (mg/L)	156	3.5 ± 1.6	1.1 - 10.0
Mg (mg/L)	122	0.60 ± 0.27	0.17 - 1.7
K (mg/L)	154	0.31 ± 0.15	0.10 - 0.90
Ca (mg/L)	158	1.5 ± 0.6	0.3 - 3.1
Al (mg/L)	19	0.11 ± 0.03	0.058 - 0.17
Mn (mg/L)	68	0.012 ± 0.005	0.010 - 0.030
Fe (mg/L)	50	0.14 ± 0.10	0.010 - 0.61
Cl (mg/L)	156	6.2 ± 3.6	1.4 - 22
SO_4-MTB (mg/L)	157	3.8 ± 1.5	1.0 - 9.0
SO_4-IC (mg/L)	10	2.2 ± 0.6	1.4 - 3.0
NOx (mg/L)	128	0.061 ± 0.061	0.001 - 0.27
DOC (mg/L)	17	5.3 ± 2.0	1.8 - 9.3
T-Alk (mg/L)	146	1.8 ± 1.1	0.5 - 6.0
G-Alk (mg/L)	14	0.85 ± 0.71	-0.30 - 2.2

Table 1-26

River: Pipers Hole, NFLD; River No. 26

Period of record: 231, 1966 to 119, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		25.9 ± 3.7	20.8 - 32.8
pH	183	6.3 ± 0.4	4.7 - 7.3
conductivity (uS)	178	25 ± 7	15 - 73
turbidity (JTU)	168	0.79 ± 0.90	0.10 - 9.0
colour (Hazen units)	184	36 ± 17	5 - 100
Na (mg/L)	178	2.4 ± 1.1	1.3 - 13.0
Mg (mg/L)	158	0.42 ± 0.11	0.20 - 0.92
K (mg/L)	178	0.24 ± 0.15	0.10 - 1.00
Ca (mg/L)	178	1.69 ± 0.52	0.80 - 5.0
Al (mg/L)	46	0.074 ± 0.025	0.010 - 0.12
Mn (mg/L)	91	0.019 ± 0.015	0.010 - 0.10
Fe (mg/L)	75	0.23 ± 0.11	0.050 - 0.50
Cl (mg/L)	169	3.7 ± 1.8	1.2 - 21
SO_4-MTB (mg/L)	170	2.3 ± 0.8	1.0 - 6.9
SO_4-IC (mg/L)	18	1.1 ± 0.2	0.8 - 1.6
NOx (mg/L)	144	0.030 ± 0.030	0.001 - 0.14
DOC (mg/L)	48	6.3 ± 3.0	0.50 - 16.0
T-Alk (mg/L)	165	3.6 ± 1.6	0.50 - 10.0
G-Alk (mg/L)	6	2.8 ± 1.2	1.5 - 4.7

Table 1-27

River: Rocky, NFLD; River No. 27

Period of record: 218, 1966 to 116, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		11.1 ± 2.0	8.0 - 14.9
pH	204	6.2 ± 0.5	4.2 - 8.2
conductivity (uS)	206	40 ± 9	25 - 87
turbidity (JTU)	203	0.97 ± 0.80	0.10 - 5.0
colour (Hazen units)	205	69 ± 43	10 - 450
Na (mg/L)	204	4.5 ± 1.1	1.9 - 9.3
Mg (mg/L)	181	0.80 ± 0.26	0.10 - 1.8
K (mg/L)	205	0.33 ± 0.15	0.1 - 1.1
Ca (mg/L)	203	1.7 ± 0.5	0.7 - 3.8
Al (mg/L)	48	0.095 ± 0.035	0.020 - 0.19
Mn (mg/L)	94	0.025 ± 0.023	0.010 - 0.16
Fe (mg/L)	76	0.27 ± 0.13	0.020 - 0.71
Cl (mg/L)	205	7.5 ± 2.4	1.1 - 21
SO_4-MTB (mg/L)	202	3.4 ± 1.2	1.5 - 8.0
SO_4-IC (mg/L)	23	1.7 ± 0.5	0.9 - 3.2
NOx (mg/L)	144	0.013 ± 0.011	0.001 - 0.050
DOC (mg/L)	52	9.2 ± 4.4	1.0 - 24
T-Alk (mg/L)	195	3.5 ± 1.8	0 - 9.4
G-Alk (mg/L)	14	1.8 ± 1.4	-1.0 - 3.9

Table 1-28

River: Garnish, NFLD; River No. 28

Period of record: 247, 1971 to 121, 1985

Variable	n	mean ± S.D.	range
mean annual discharge (m^3/sec)		9.12 ± 0.97	7.58 - 10.7
pH	110	6.2 ± 0.4	4.8 - 7.1
conductivity (uS)	108	46 ± 12	22 - 98
turbidity (JTU)	106	0.61 ± 0.34	0.10 - 2.3
colour (Hazen units)	111	47 ± 24	5 - 140
Na (mg/L)	110	5.4 ± 1.5	2.4 - 12
Mg (mg/L)	111	0.74 ± 0.24	0.32 - 1.6
K (mg/L)	110	0.35 ± 0.17	0.10 - 1.0
Ca (mg/L)	110	2.0 ± 0.4	0.70 - 3.0
Al (mg/L)	17	0.16 ± 0.06	0.060 - 0.27
Mn (mg/L)	49	0.025 ± 0.020	0.010 - 0.13
Fe (mg/L)	34	0.18 ± 0.08	0.020 - 0.34
Cl (mg/L)	107	9.2 ± 3.4	3.9 - 20.0
SO_4-MTB (mg/L)	107	3.7 ± 1.2	2.0 - 8.0
SO_4-IC (mg/L)	11	1.8 ± 0.3	1.1 - 2.1
NOx (mg/L)	85	0.025 ± 0.022	0.001 - 0.14
DOC (mg/L)	18	7.2 ± 2.4	3.6 - 11.0
T-Alk (mg/L)	103	3.1 ± 1.5	0.5 - 9.5
G-Alk (mg/L)	5	1.9 ± 0.8	0.9 - 3.1

Table 2. Statistically significant year effects for the data of selected Newfoundland or Nova Scotia rivers, controlling for variation due to river.

TABLE A

					Year Effects																			
					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$\sqrt{Alk}$	N.S.	yr	.001	.93														−.57		−.37				
		sp	.001	.90															−.52	−.57		−.72	−.47	
		su	NS	.75																				
		wi	< .001	.93													−.53						.54	
	Nfld.	yr	< .001	.93										.30										
		sp	.005	.82																				
		su	.005	.85										.52										
		wi	< .001	.90		−.54		−.58	−.32				.46		−.29	−.49			−.51	−.34	−.35			
$\sqrt{DOC}$	N.S.	yr	< .001	.92										.76		.55		.45	.47		−.33	−.21		
		sp	.025	.82						.69								.66						
		su	< .001	.92													.75			−.61	−.26			
		wi	< .001	.96										.84				.55				−.36		
	Nfld.	yr	< .001	.89															.95	.40				
		sp	< .001	.84				.80									.45	1.21	.63	.31				
		su	< .001	.83												.88	.92	1.09		.38				
		wi	.05	.64														.74	.44					

					Year Effects																			
					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$\sqrt{SO_4}$	N.S.	yr	.001	.65			−.37			−.36	−.34			.31	−.34	−.31	−.37		−.25	−.20	−.29	−.25		
		sp	.025	.48						−.45	−.52			−.89				−.38	−.34	−.39		−.38	−.35	
		su	.025	.62			−.36													−.30		−.29		
		wi	.005	.67			−.58			−.42	−.45		−.44						−.32	−.35		−.4	−.32	
	Nfld.	yr	< .01	.59								.25												
		sp	NS	.37																				
		su	.001	.32						−.39														
		wi	.05	.49								−.42												
$\sqrt{SO_4}$ IQR	N.S.	yr	< .001	.63								.50		1.28									−.40	
		sp	< .001	.64																				
		su	< .001	.53														−.62						
		wi	.025	.47		.79						1.26												
	Nfld.	yr	< .001	.62						−.40					−.41	−.57	−.61		−.57	−.56	−.57	−.64	−.40	
		sp	.001	.53			.80		.72				.66	.92										
		su	.001	.49			−.99							−.79	−.81	−.77	−1.19			−.95		−1.102		
		wi	NS	.35												−.55								

					Year Effects																			
					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
pH	N.S.	yr	< .001	.98							−.18	−.24		.29			.60						.13	
		sp	.05	.95																				
		su	< .001	.97					−.25	−.31	−.41						−.40				−.30			
		wi	.05	.93								−.43												
	Nfld.	yr	< .001	.88					−.27		−.30	−.34	−.23											
		sp	< .001	.81			−.31	−.40	−.24	−.35	−.22	−.34	.27											
		su	< .001	.68							−.42													
		wi	< .001	.73						−.31	−.70	−.32												

<u>Table 3.</u> Before and after analysis of medians and sample sizes of Nova Scotia and Newfoundland rivers for sulfate and dissolved organic carbon.

“Rivers”

“7” “11” “12” “13” “14” “16” “17” “18” “19”

“NS SO_4 medians before and after yr 15”

	< 15 >	= 15
7	3.0940	2.868
11	2.9330	2.639
12	3.4660	3.627
13	3.3925	3.947
14	0.0	3.708
16	3.1880	3.488
17	2.5690	3.133
18	3.3660	3.336
19	3.1175	2.513

“NS SO_4 sample sizes before and after yr 15”

	< 15 >	= 15
7	138	52
11	56	49
12	109	51
13	36	47
14	0	285
16	49	69
17	53	47
18	63	47
19	68	49

"Rivers"

"7" "11" "12" "13" "14" "16" "17" "18" "19"

"NFLD SO_4 medians before and after yr 15"

	< 15 >	= 15
20	1.7220	0.0
21	2.2135	1.9190
22	2.5940	2.6870
23	1.9270	1.9830
25	2.7900	2.6270
26	1.6660	1.5635
27	2.1505	1.6800
28	2.2270	1.8490

"NFLD SO_4 sample sizes before and after yr 15"

	< 15 >	= 15
20	105	0
21	102	51
22	157	44
23	21	18
25	130	25
26	123	46
27	152	49
28	83	23

```
        "Rivers"

        "7" "11" "12" "13" "14" "16" "17" "18" "19"

        "NS DOC medians before and after yr 15"

         < 15 >    = 15
   7     8.95       6.70
  11     9.95       5.55
  12      0.0      11.00
  13      0.0      13.80
  14      0.0       7.70
  16      0.0       7.10
  17      0.0       8.70
  18      0.0       5.50
  19     6.00      3.70


        "NS DOC sample sizes before and after yr 15"

         < 15 >    = 15
   7     26         45
  11     10         34
  12      1         29
  13      2         30
  14      0        290
  16      2         41
  17      4         31
  18      2         31
  19     17         40
```

“Rivers”

“7” “11” “12” “13” “14” “16” “17” “18” “19”

“NFLD DOC medians before and after yr 15”

	< 15 >	= 15
20	0.0	0.0
21	10.25	6.40
22	10.40	5.80
23	0.0	5.30
25	0.0	5.35
26	9.75	5.15
27	13.00	6.90
28	0.0	7.00

“NFLD DOC sample sizes before and after yr 15”

	< 15 >	= 15
20	0	0
21	12	44
22	16	37
23	1	14
25	1	16
26	10	38
27	11	41
28	1	17

Figure 1. Location of the study rivers. The key to river numbers is as follows:

River number 1: Oromocto River, N.B.
2: Salmon River
3: Lepreau River
4: Pointe Wolfe River
5: Carruthers River, P.E.I.
6: Dunk River
7: Medway River, N.S.
8: St. Mary's River
9: Meteghan River
10: Avon River
11: Kelley River
12: Tusket River
13: Roseway River
14: Rodger's Brook
15: Whiteburn Brook
16: Lehave River
17: Liscomb River
18: Clam Harbour River
19: Wallace River
20: Harry's River, Nfld.
21: Indian River
22: Exloits River
23: Grey River
24: Grandy River
25: Isla Aux Morts River
26: Pipers Hole River
27: Rocky River
28: Garnish River

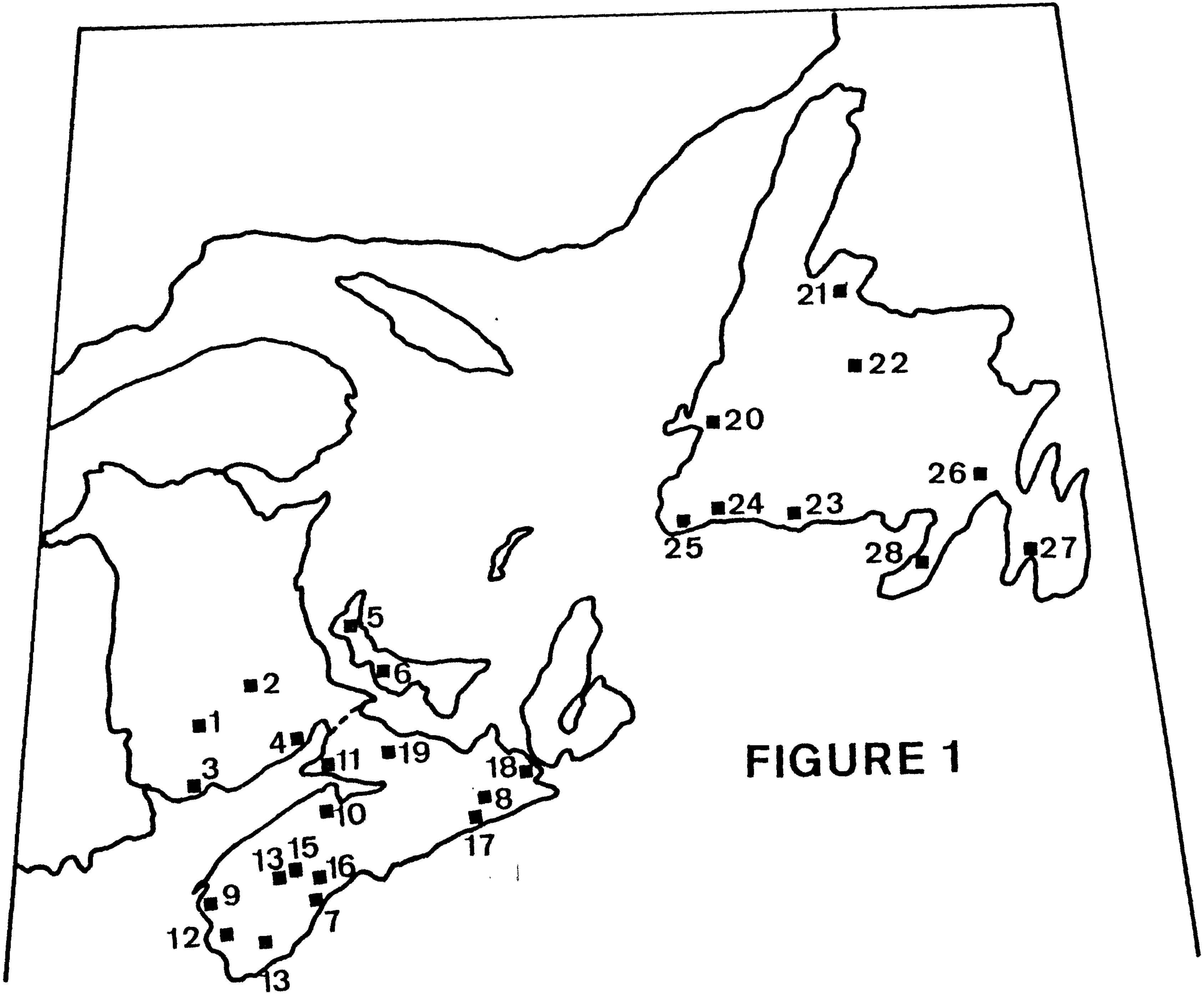
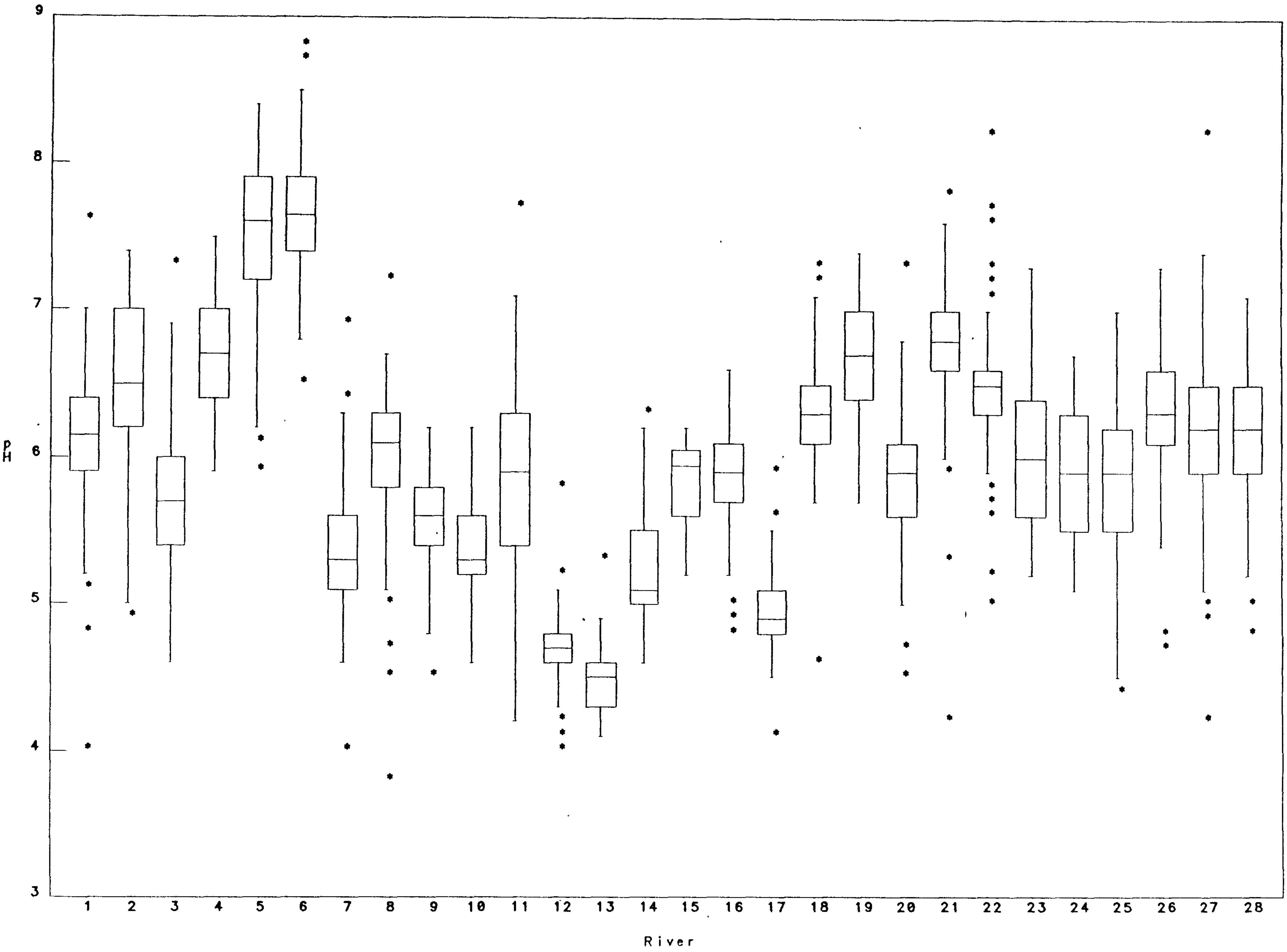


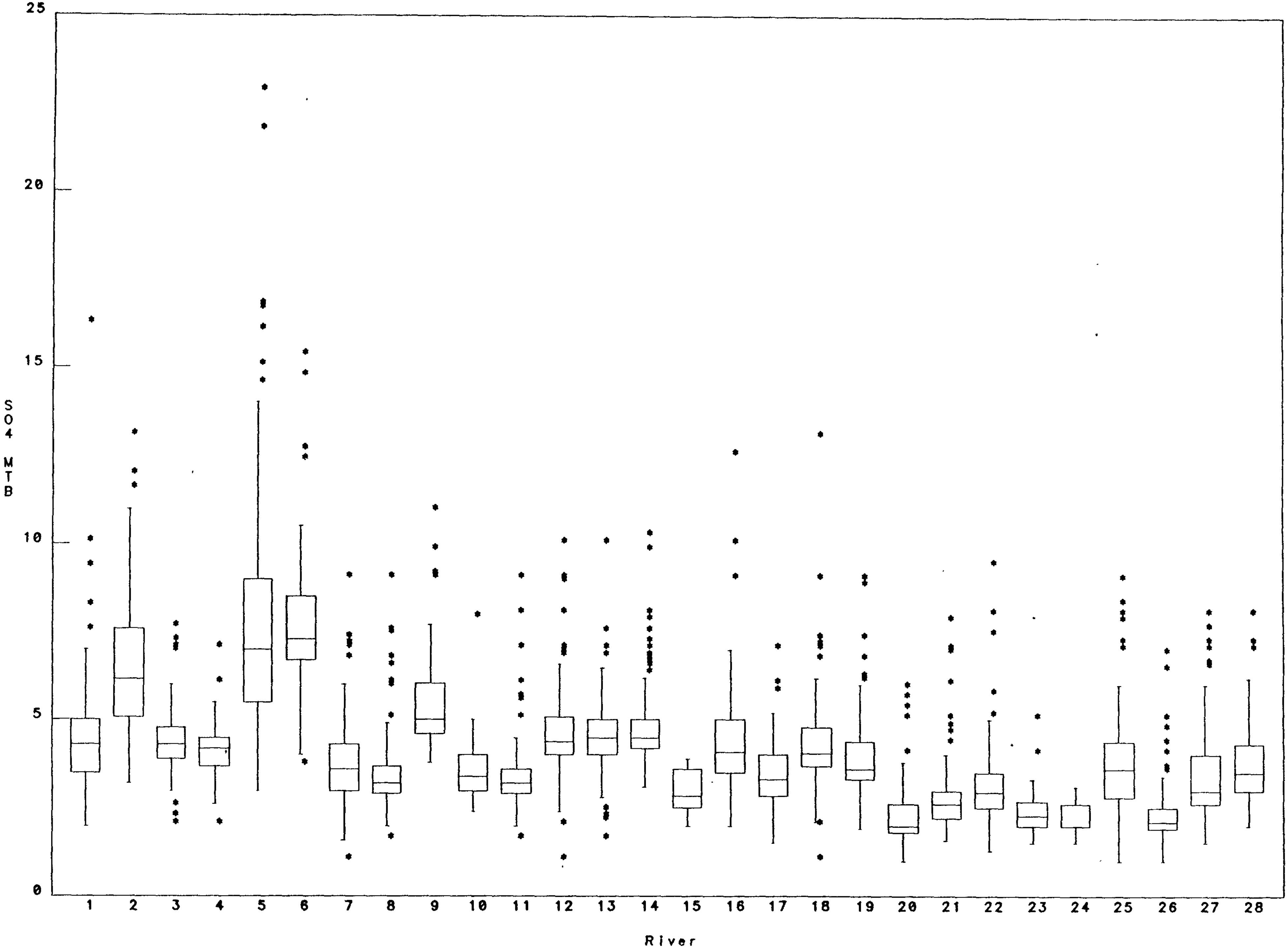
FIGURE 1

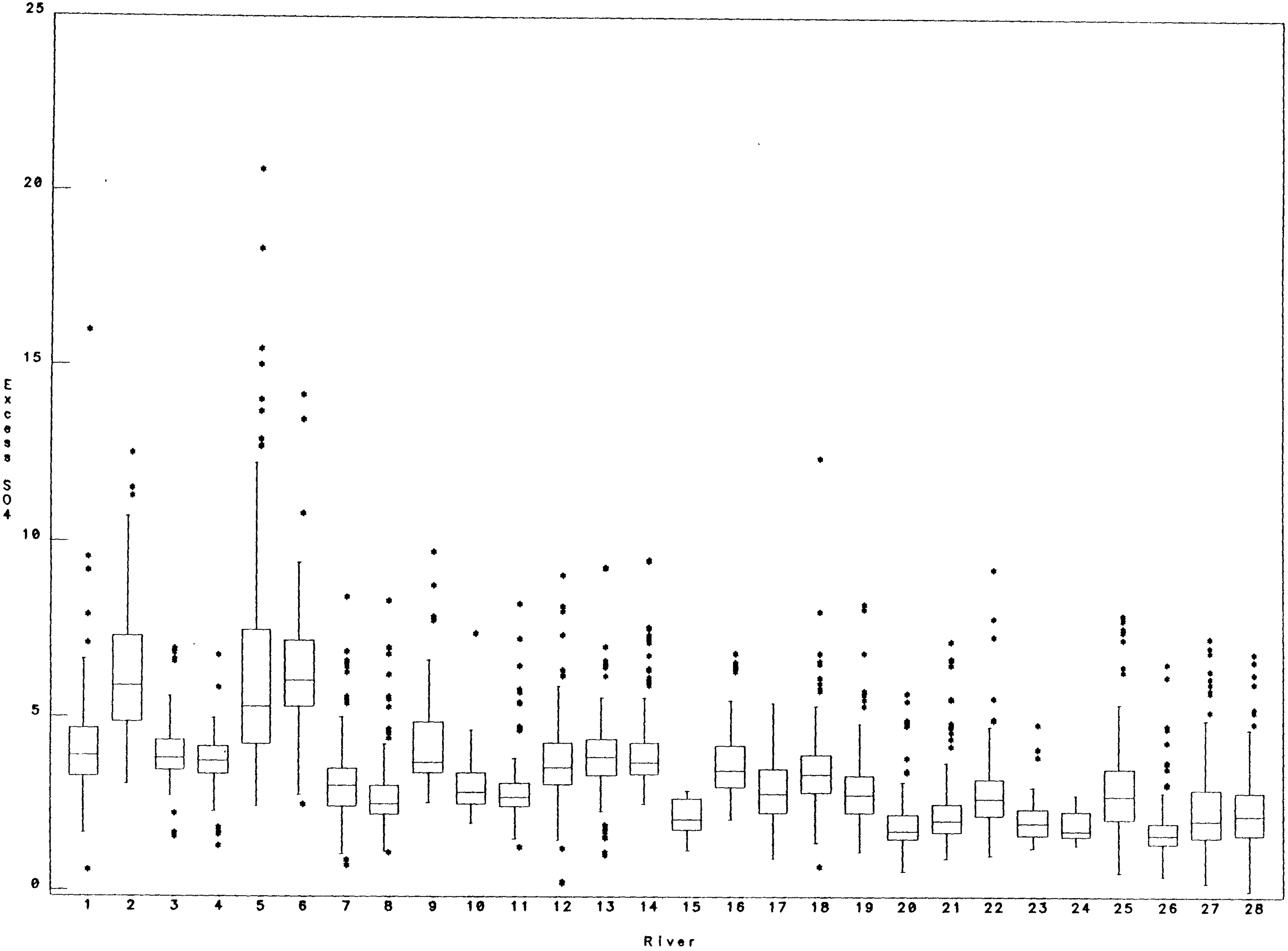
Figure 2 (a-e). Box and whisker plot comparisons of the rivers. a) pH; b) sulfate-MTB; c) excess sulfate calculated by chloride ratio; d) total alkalinity; e) dissolved organic carbon.

Box and whisker plots of pH by river



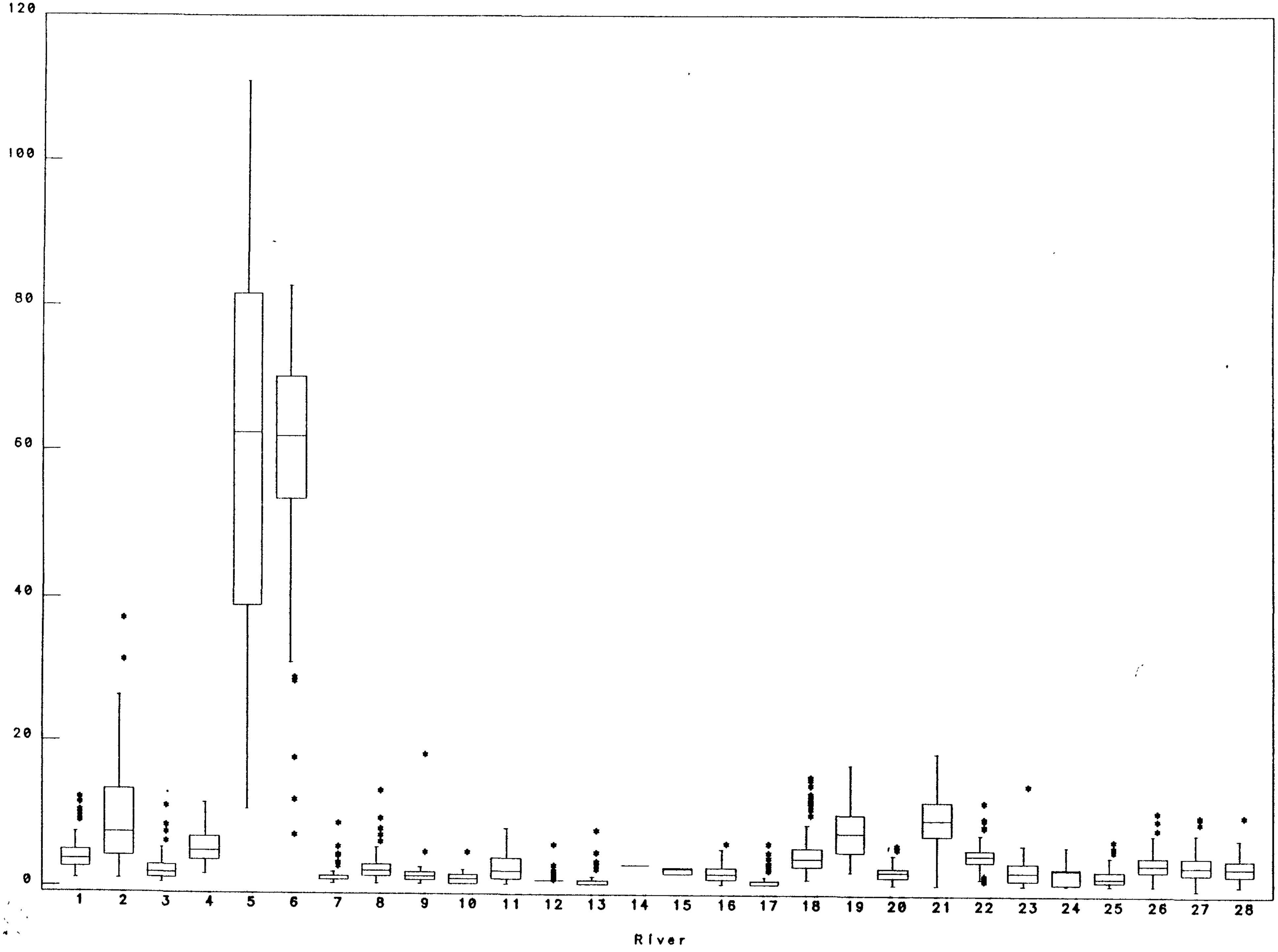
Box and whisker plots of SO4 MTB





Box and whisker plots of Excess SO4 (Cl)

Box and whisker plots of TAL



Box and whisker plots of DOC

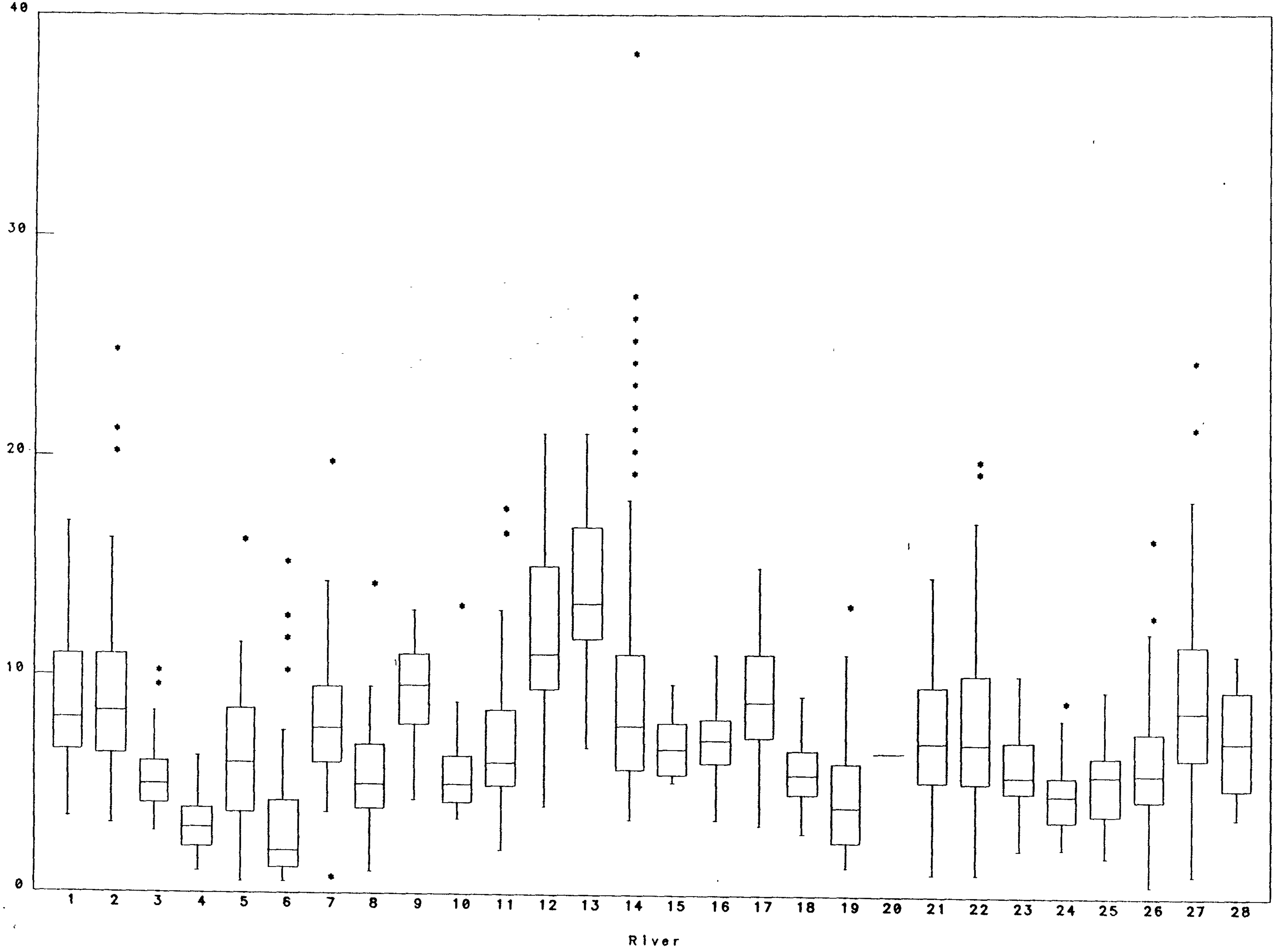
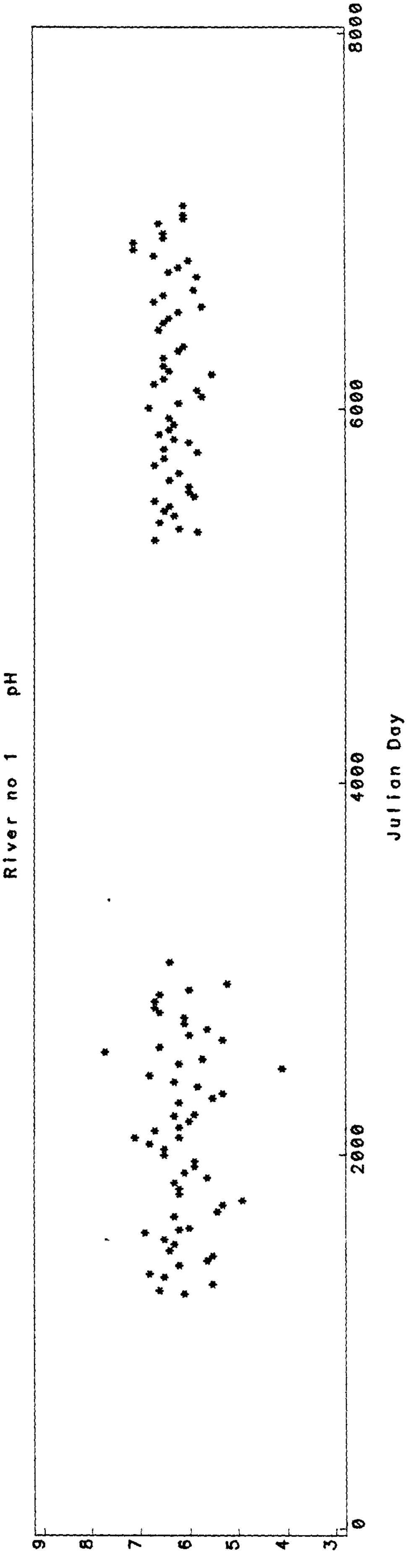


Figure 3. Scatter plots of pH versus time for the study rivers.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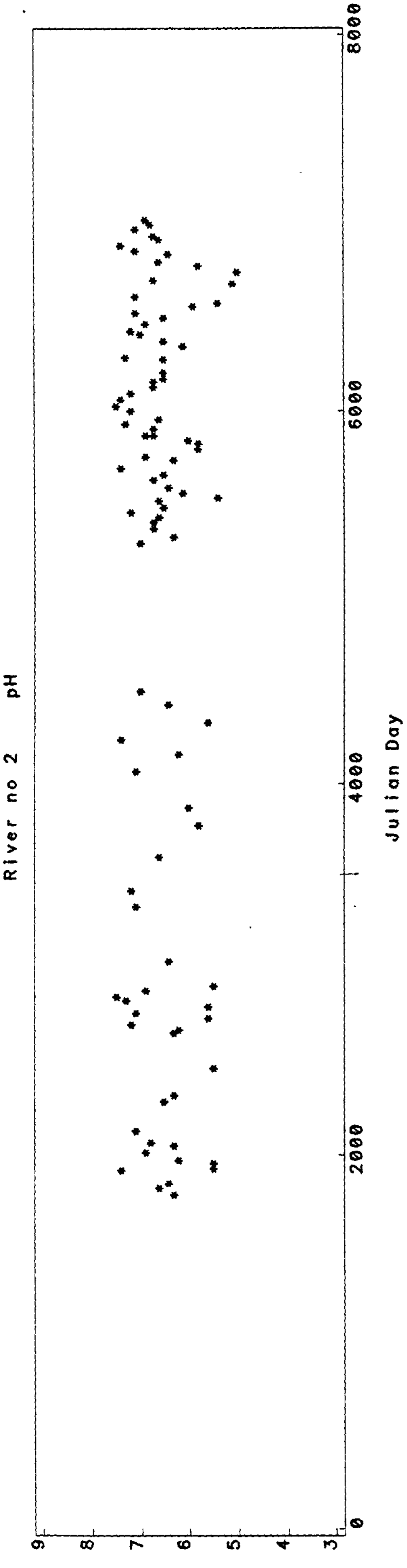
9
8
7
6
5
4
3
0
2000
4000
6000
8000
Julian Day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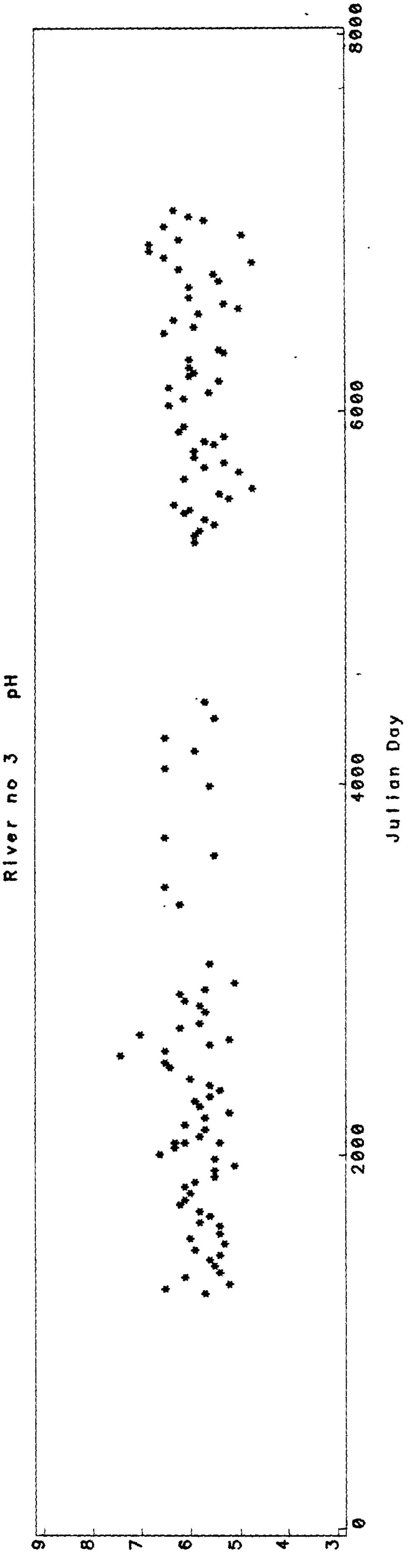
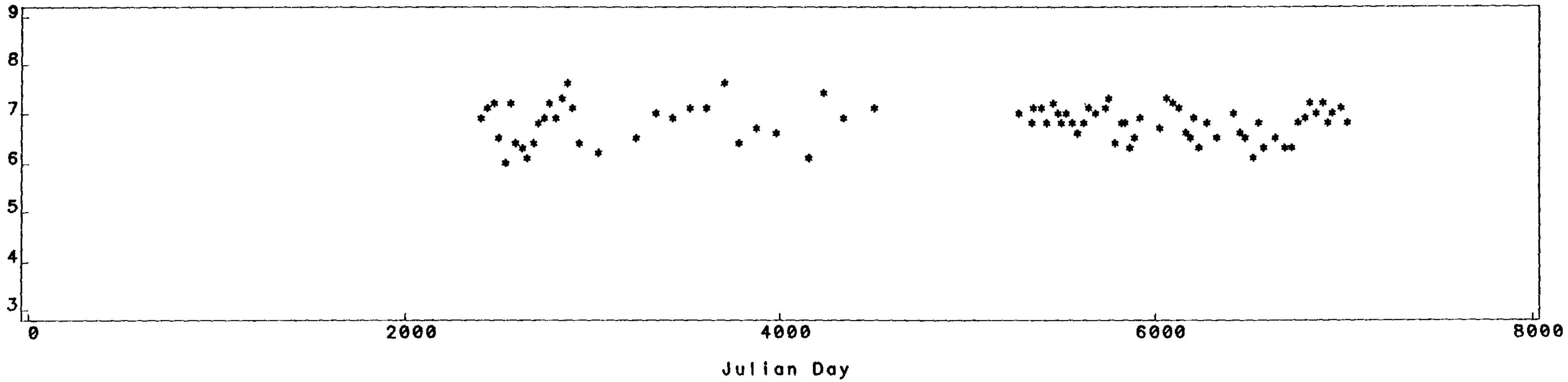
8
7
6
5
4
3
0
2000
4000
6000
8000
Julian Day


River no 3 pH
9
8
7
6
5
4
3
0
2000
4000
6000
8000
Julian Day



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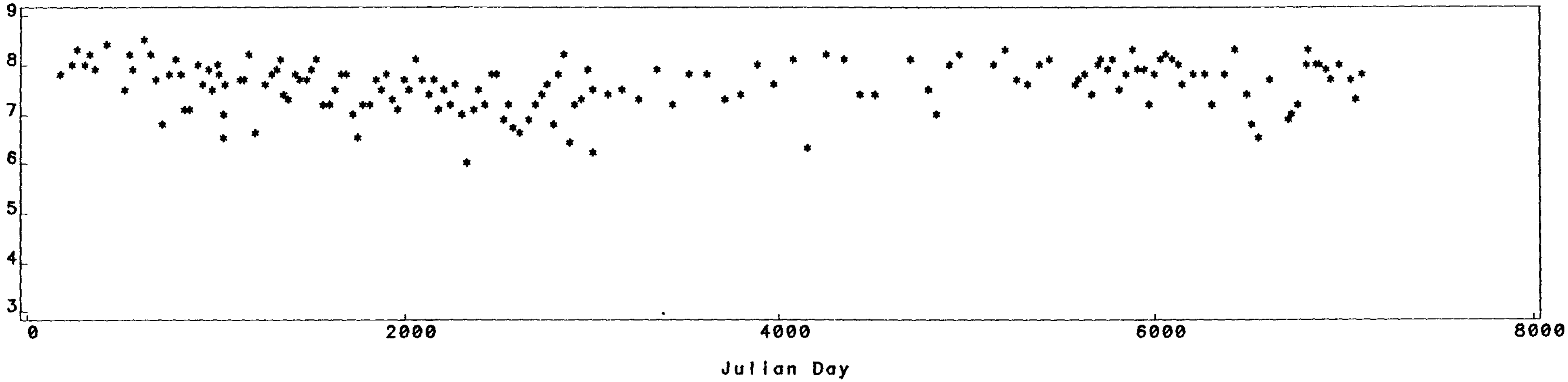
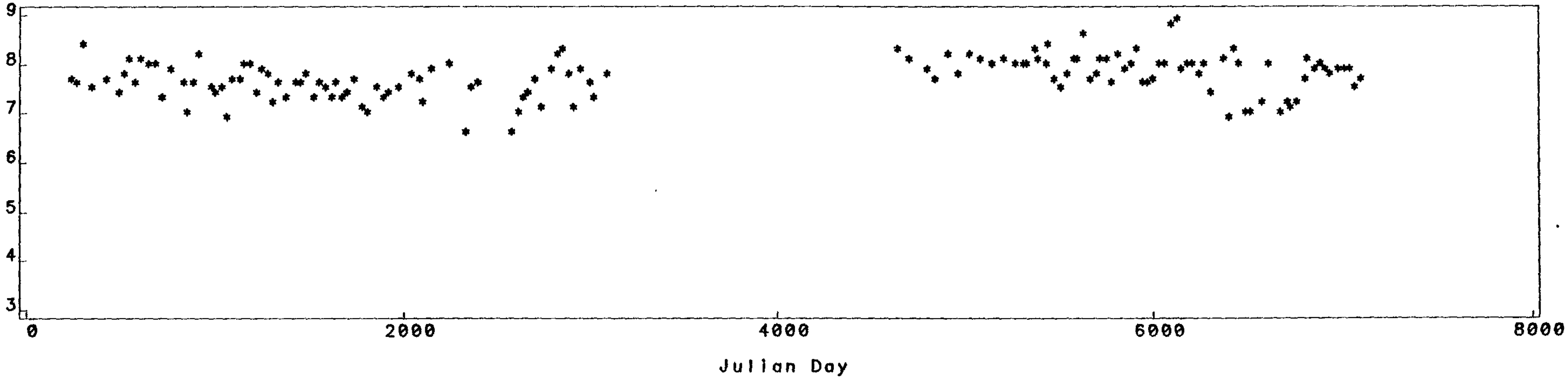


River no 5 pH



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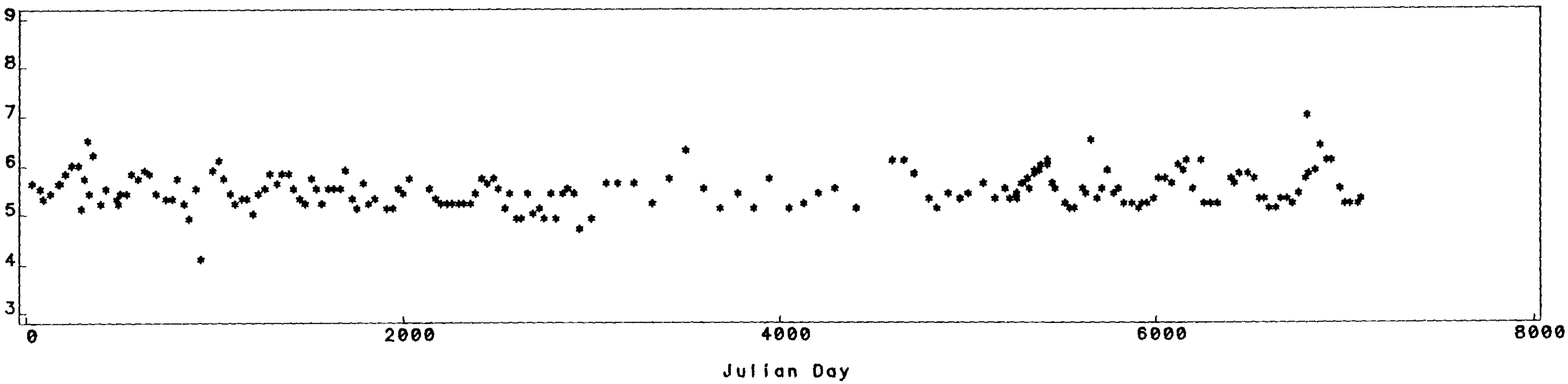
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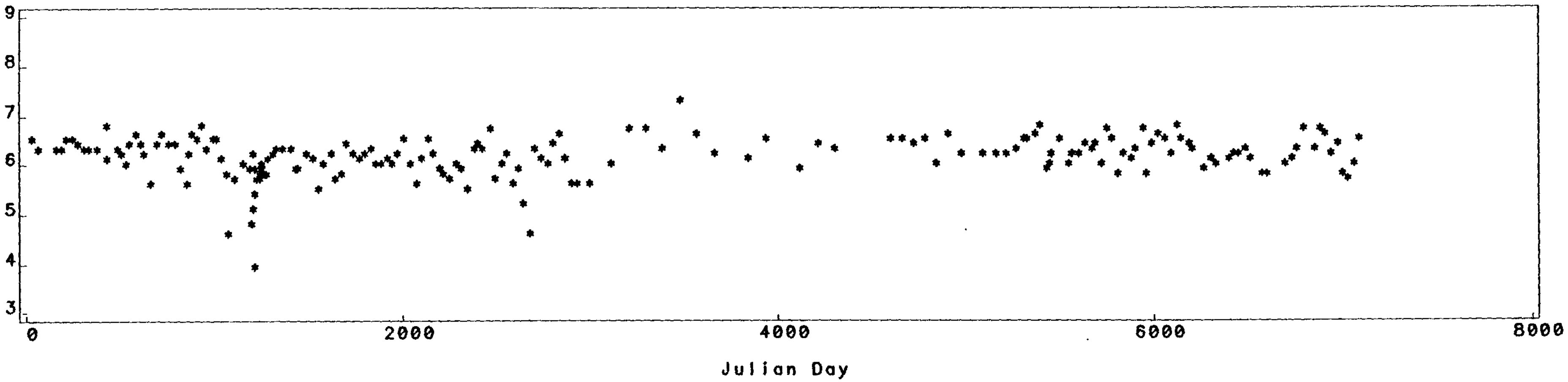
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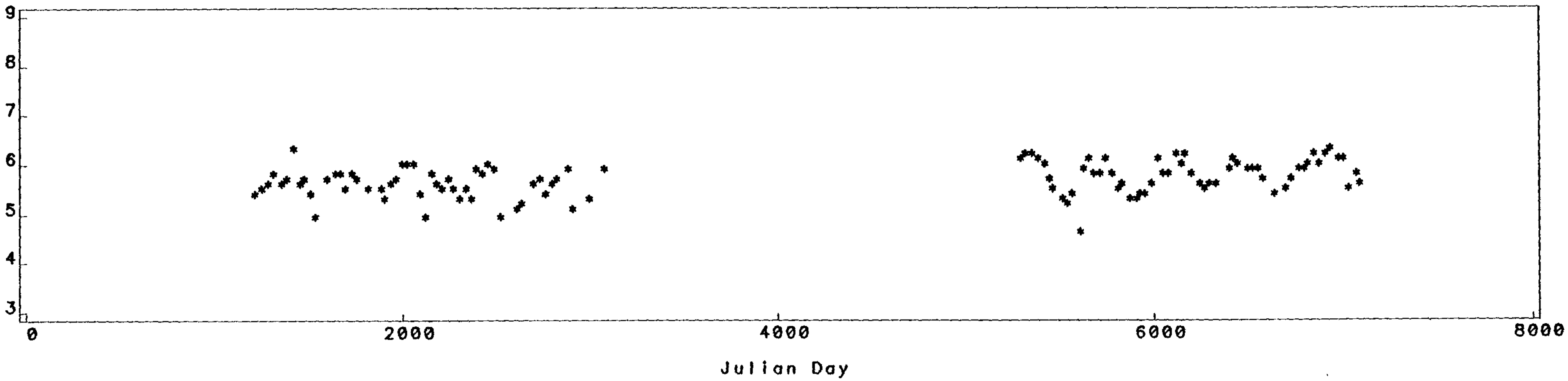
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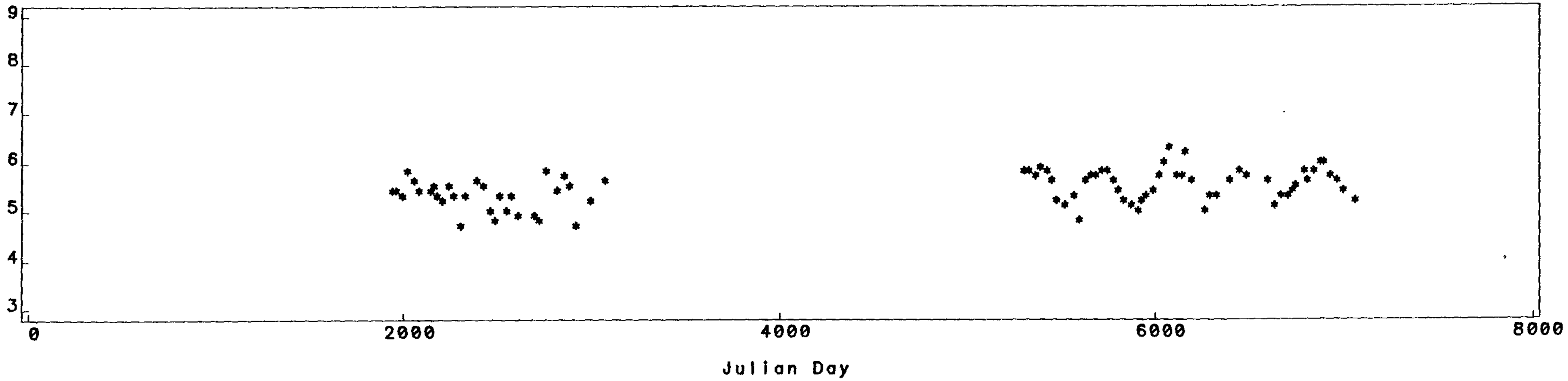

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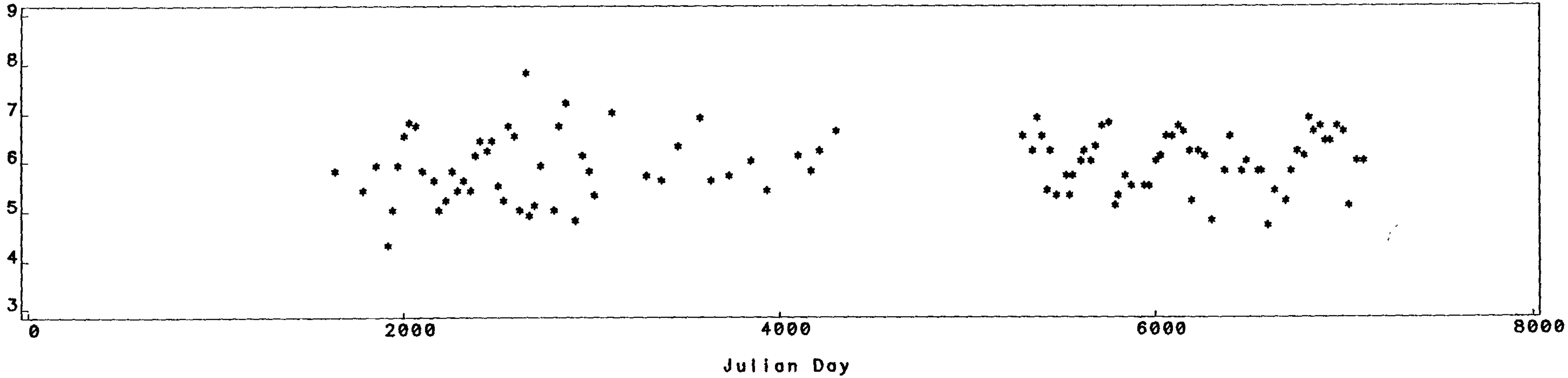

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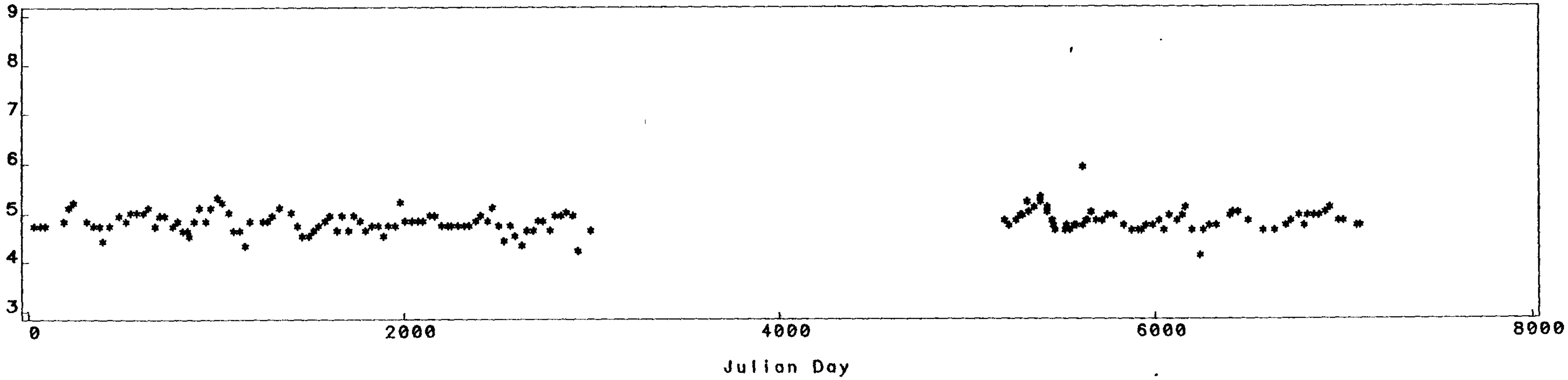

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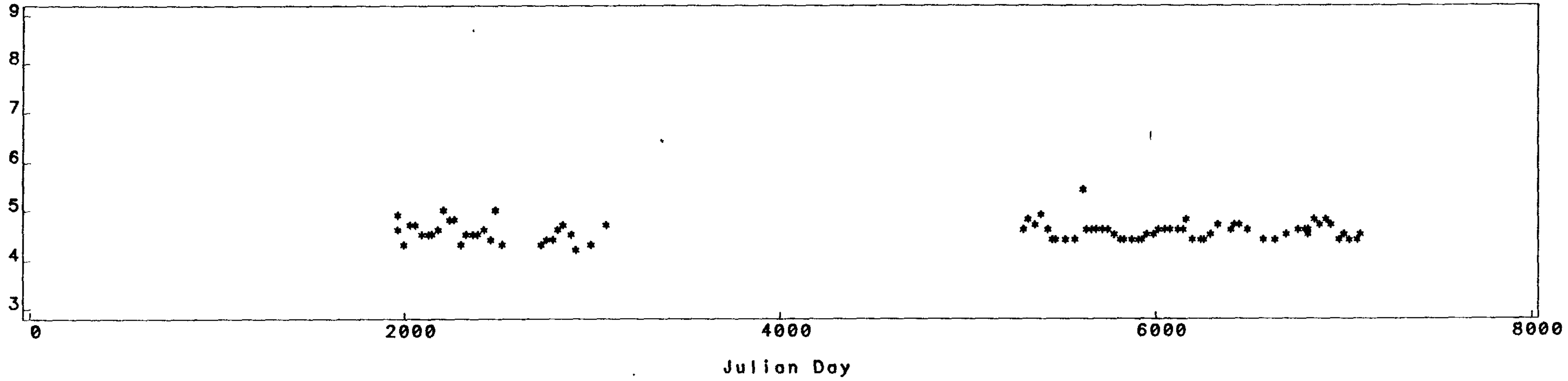

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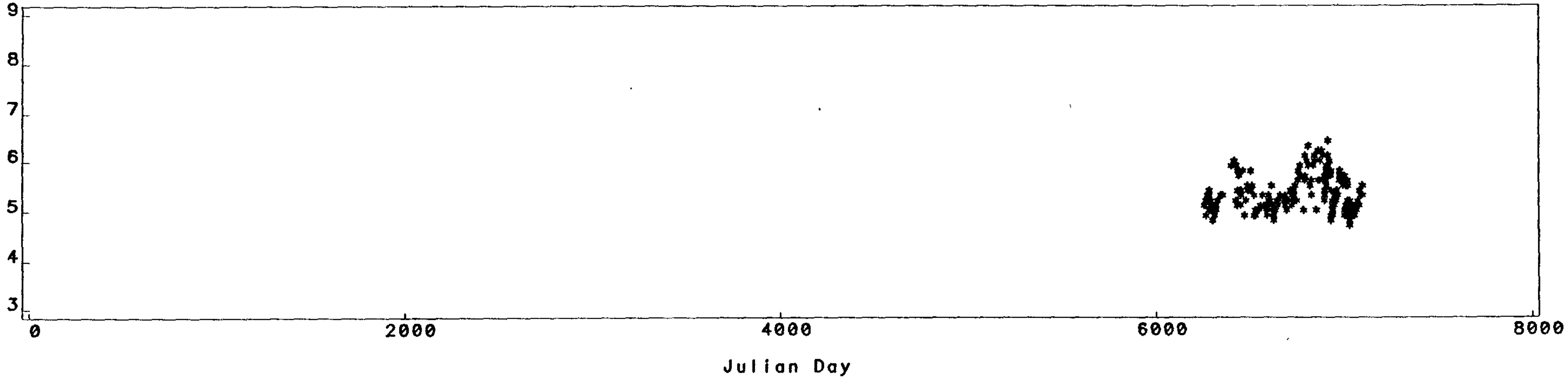

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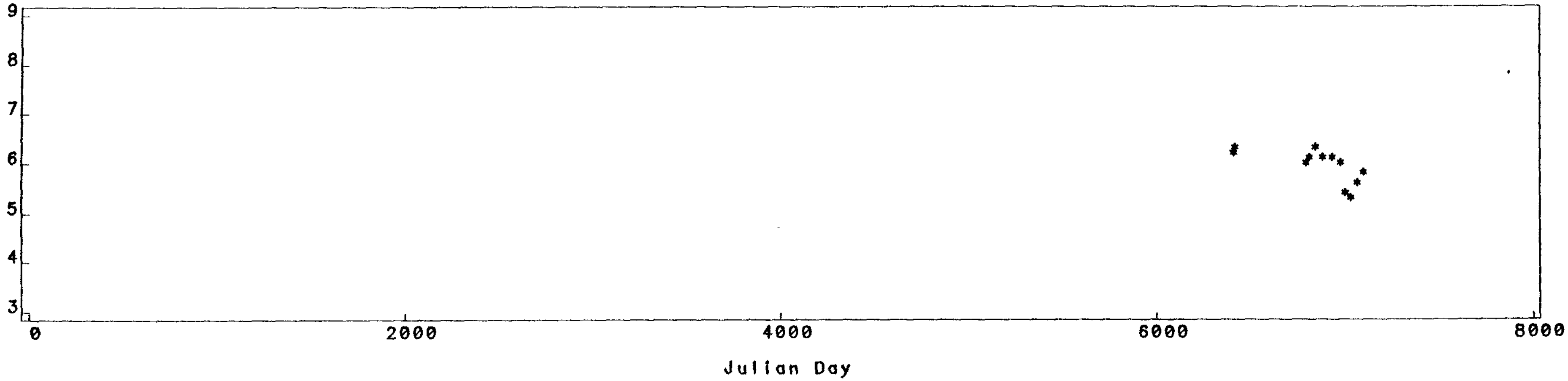

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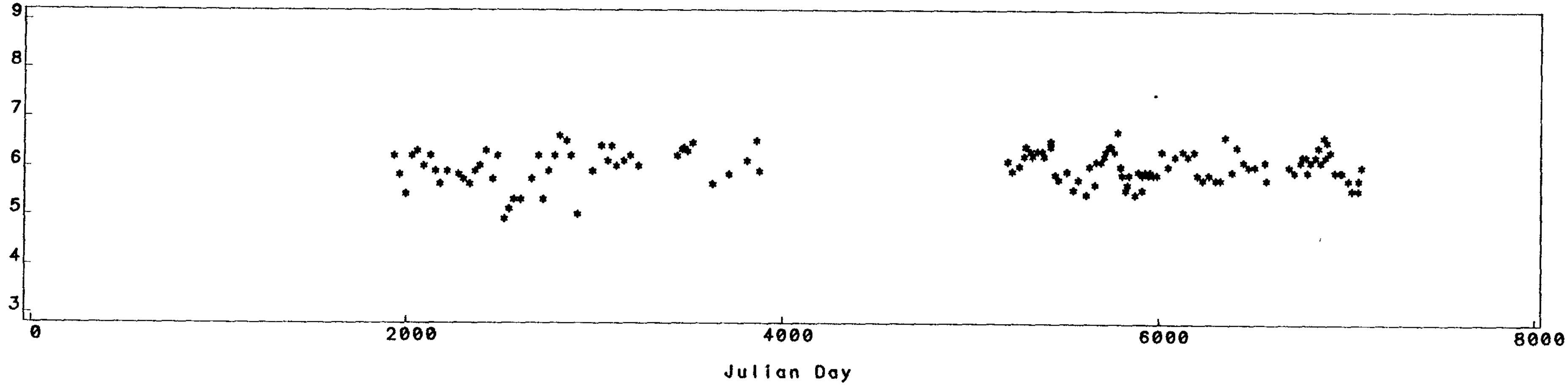

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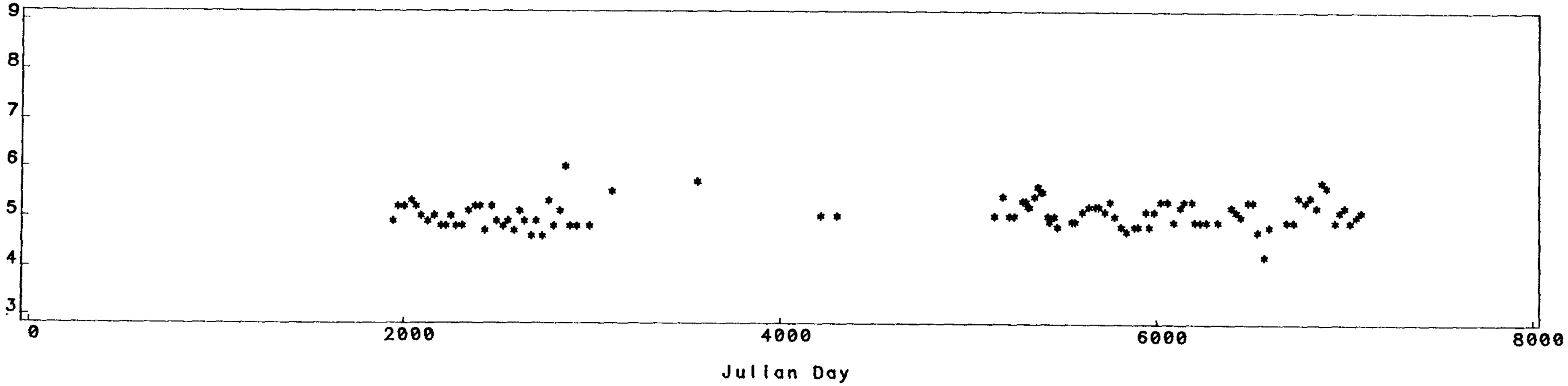

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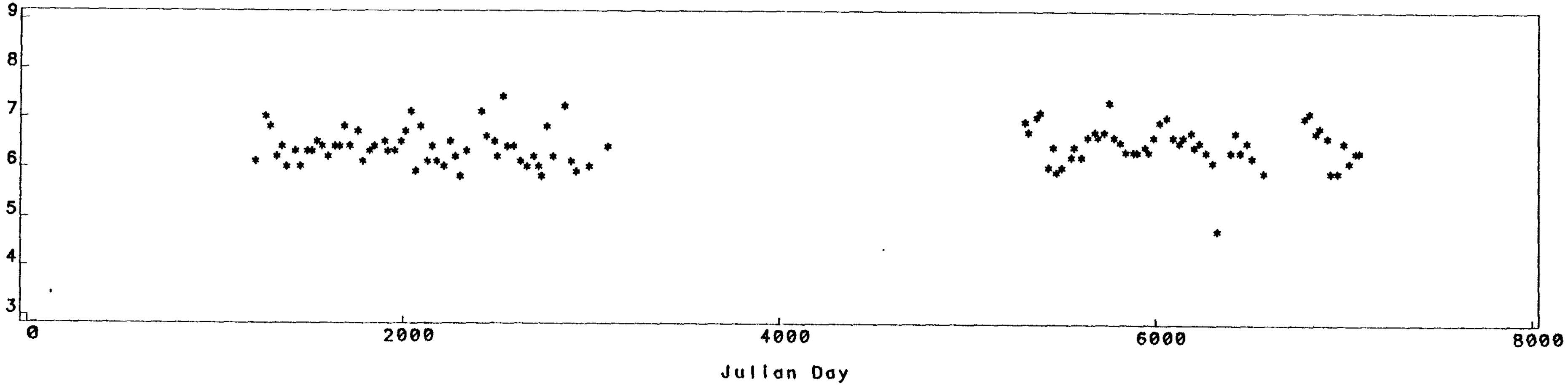

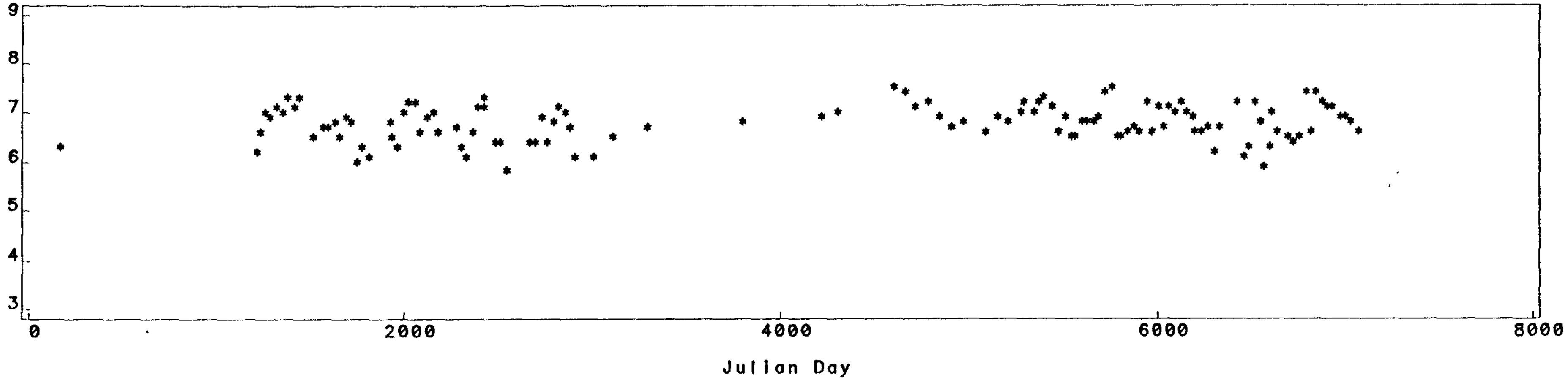

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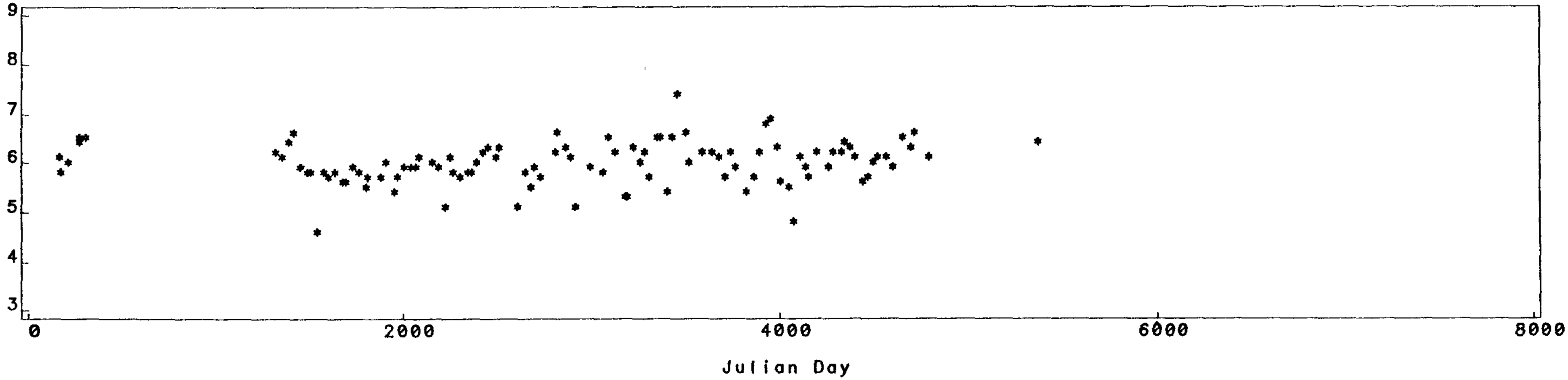

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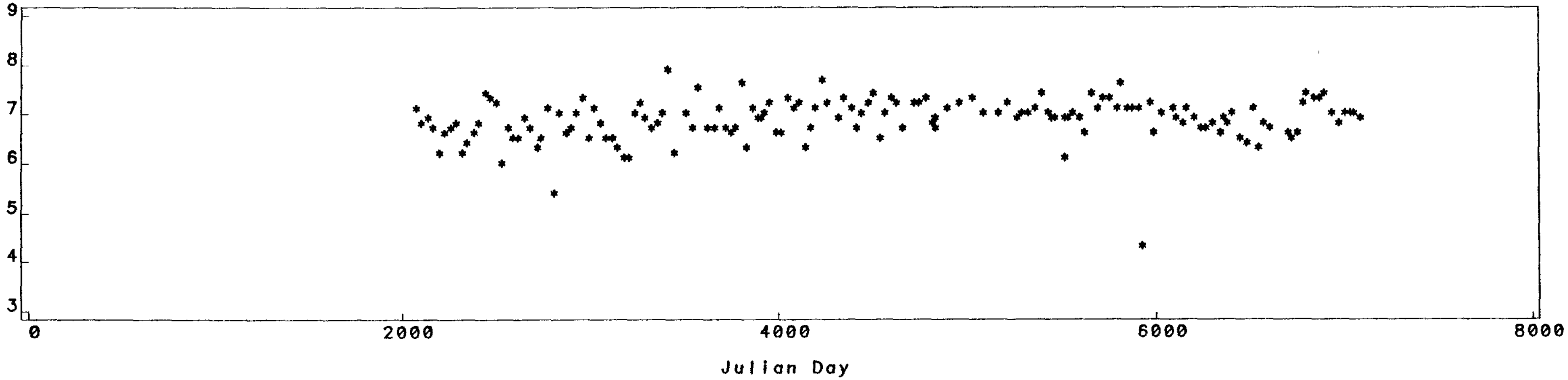
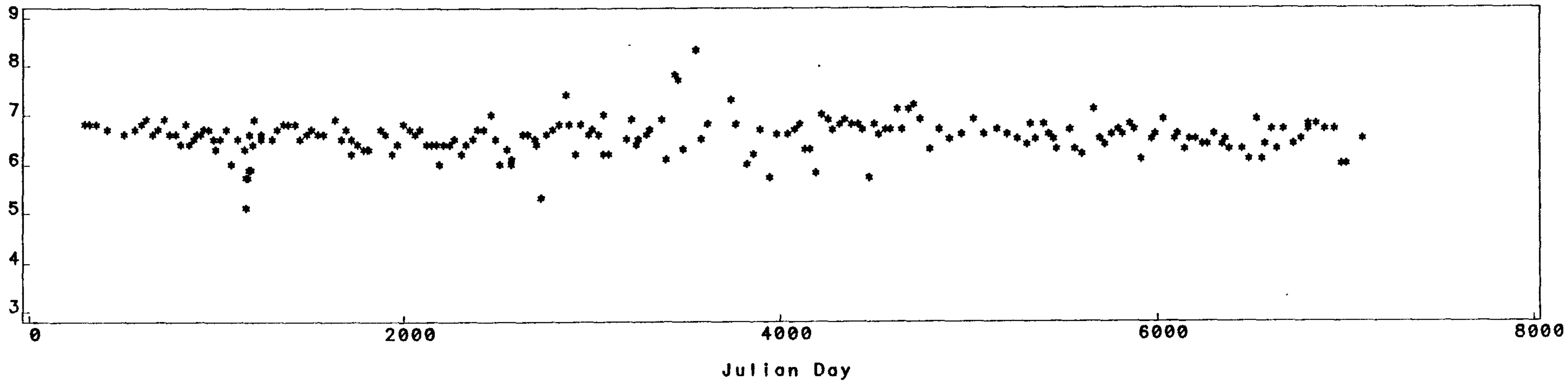


River no 21 pH

River no 22   pH



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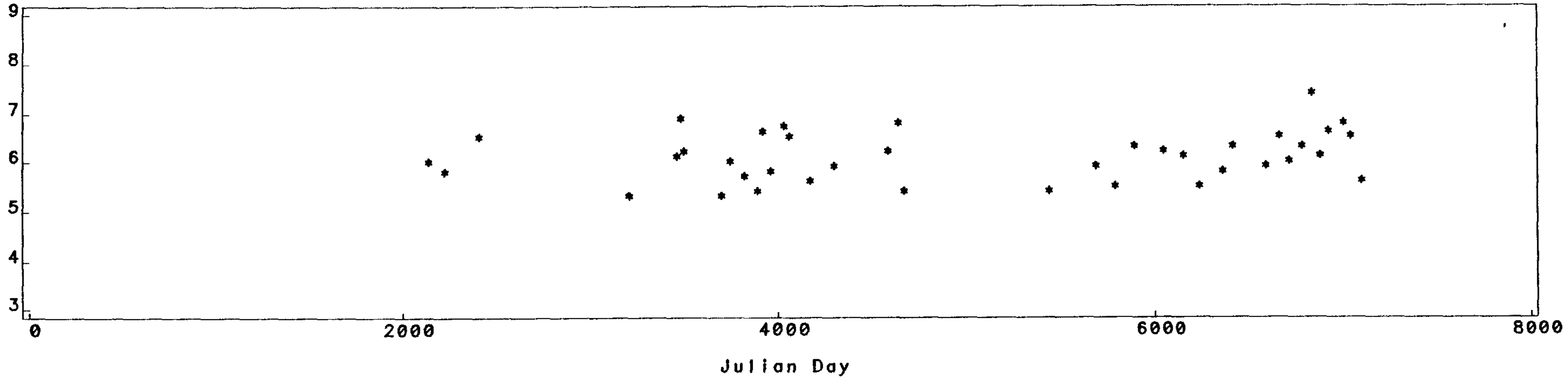

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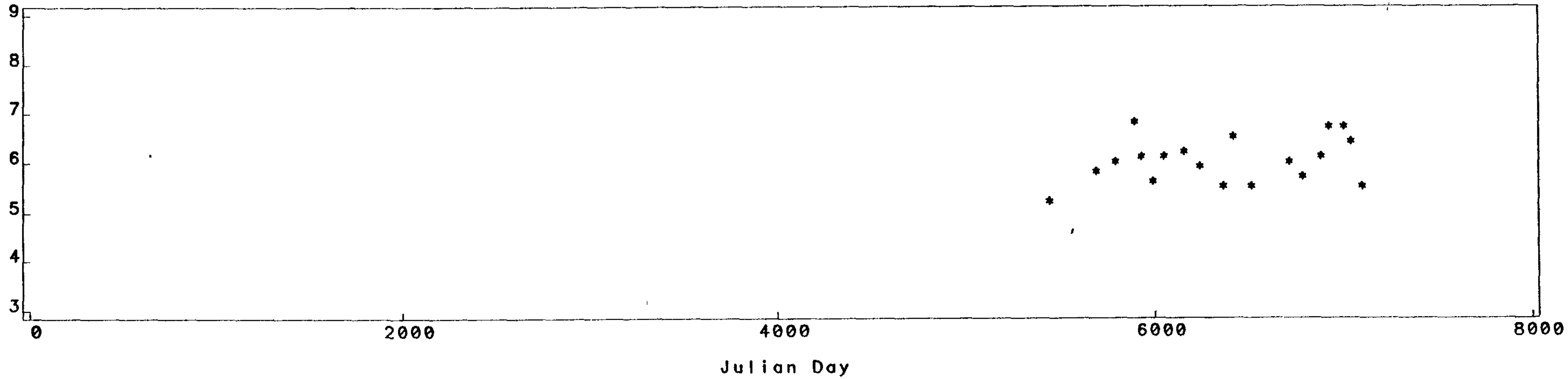

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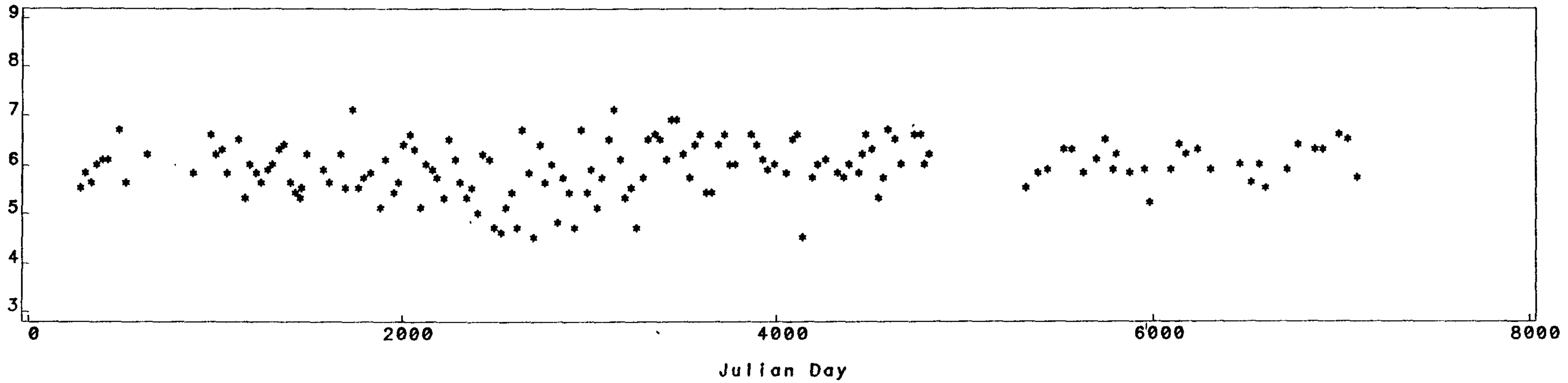

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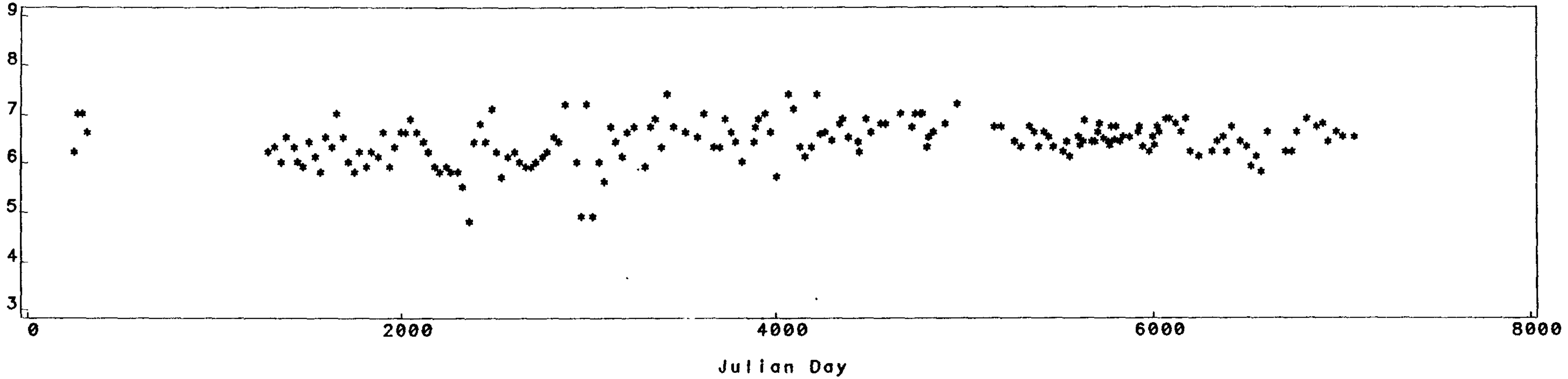

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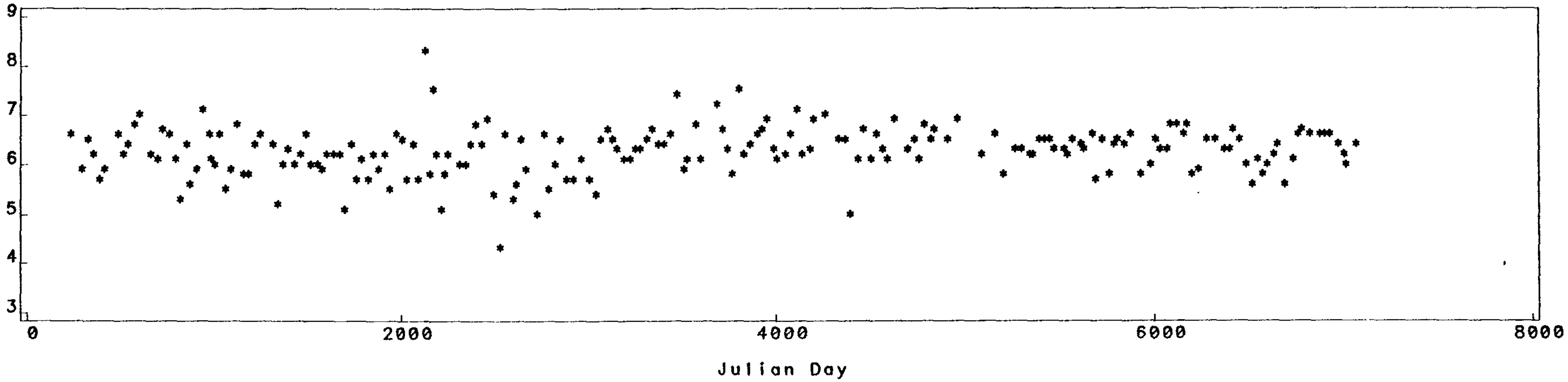

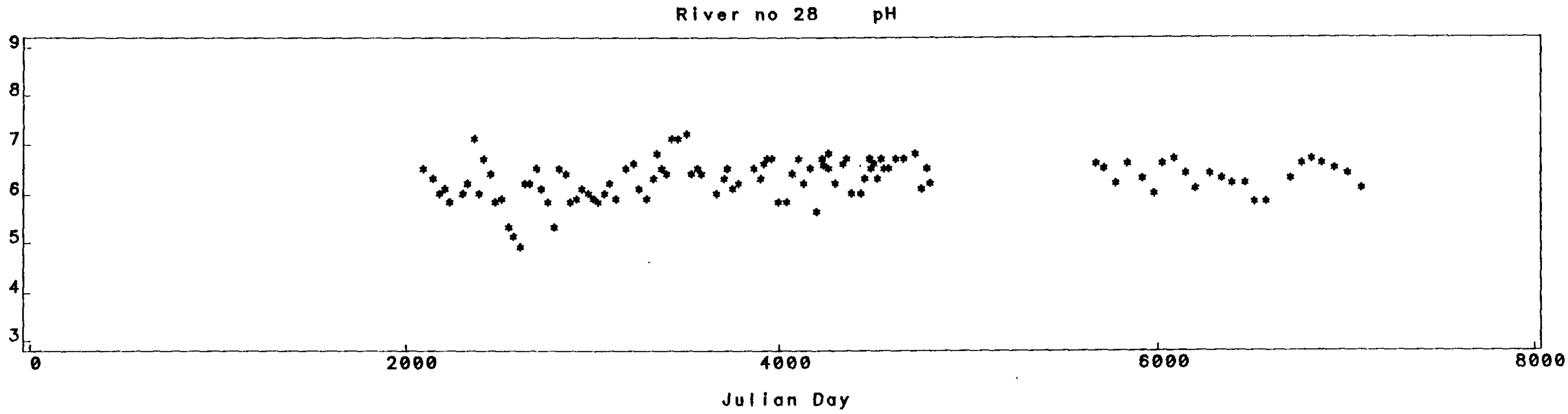
River no 28 pH
9
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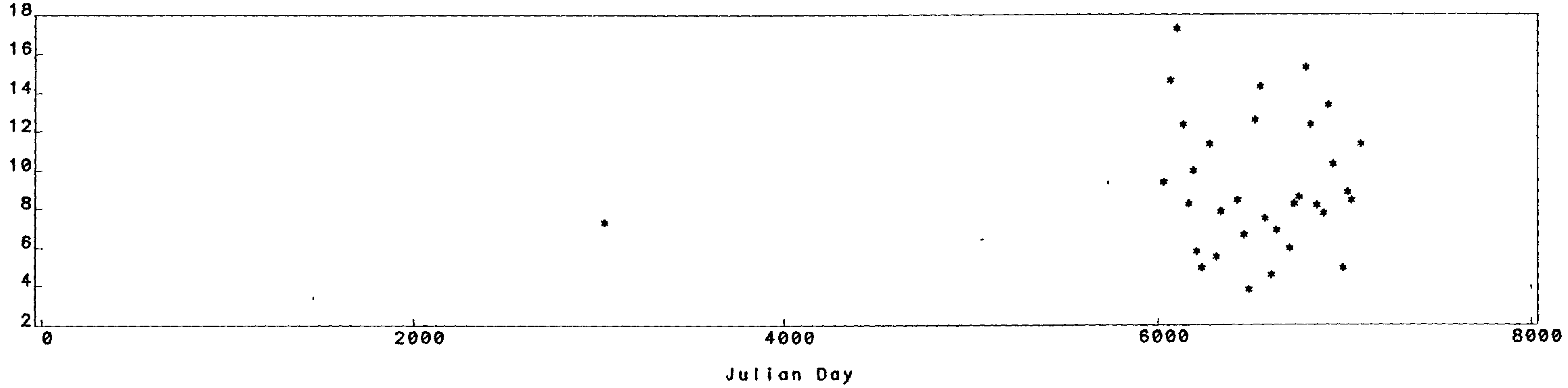
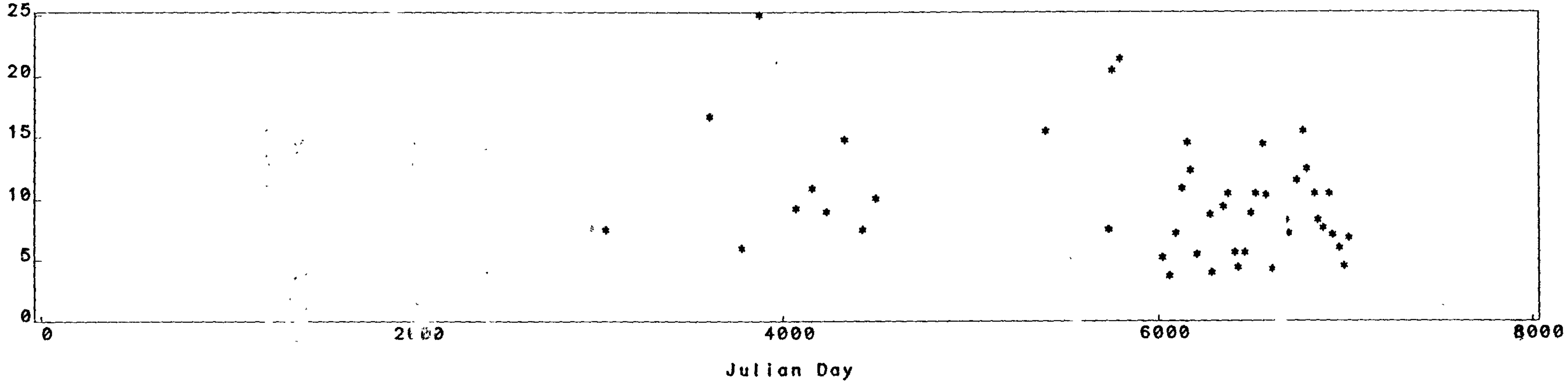
Julian Day

Figure 4. Scatter plots of dissolved organic carbon versus time for the study rivers.

River no 1 DOC



River no 2 DOC



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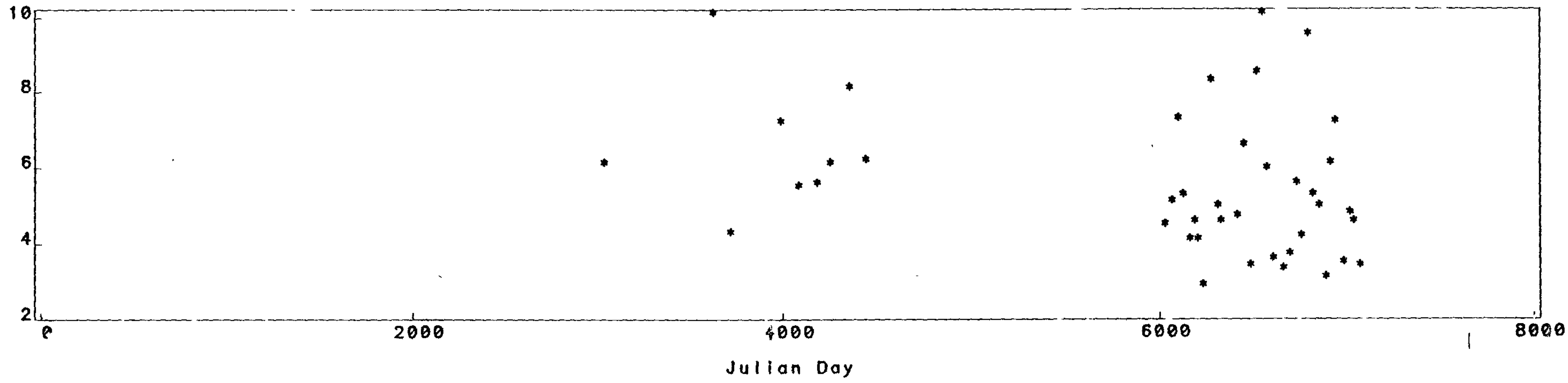

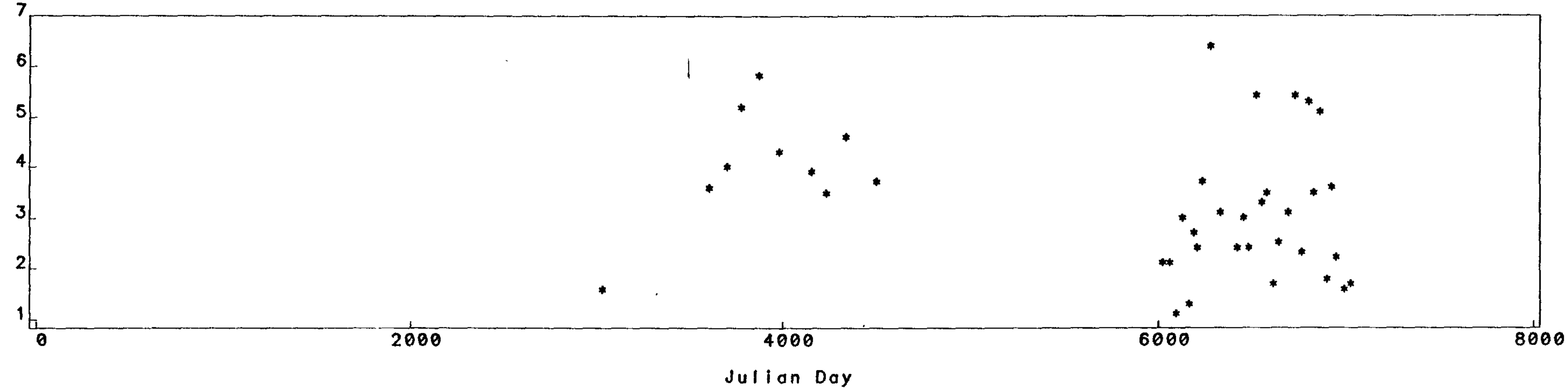
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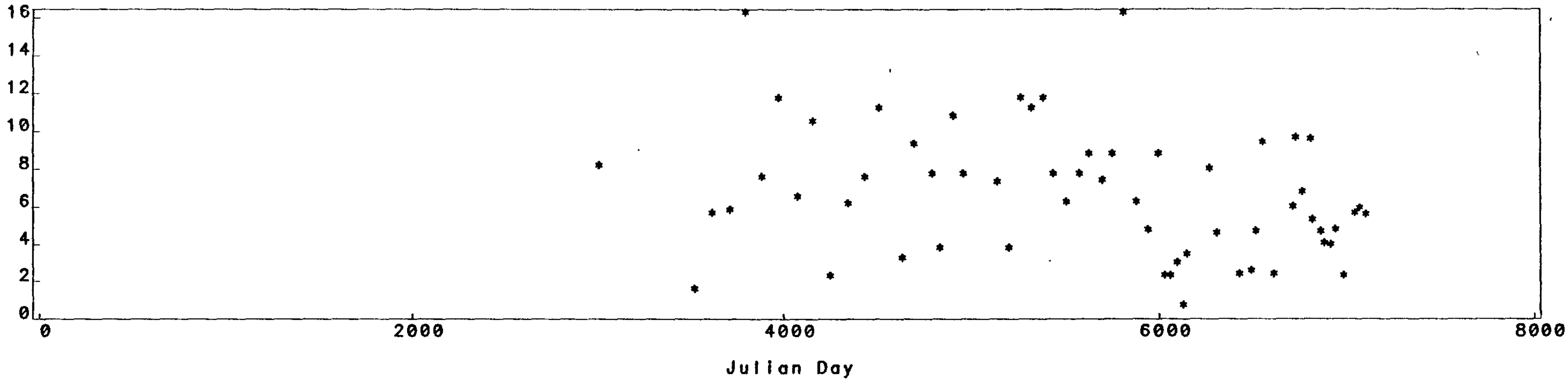
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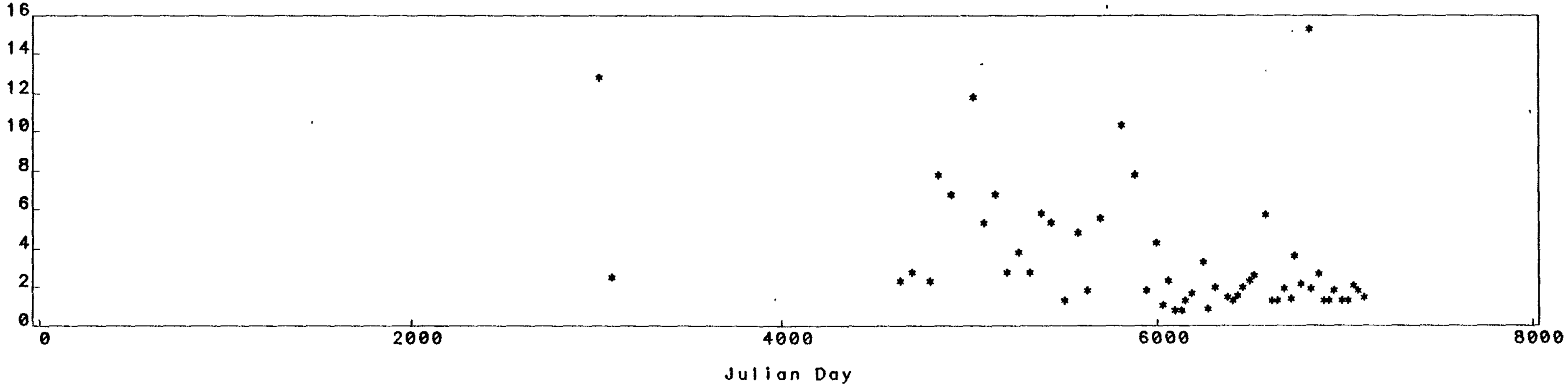
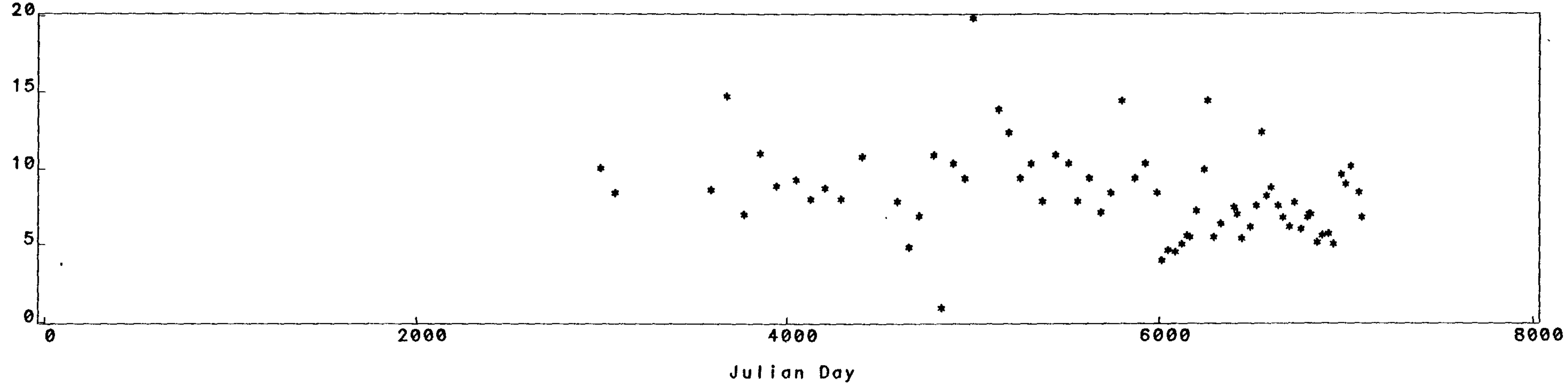

River no 6 DOC

River no 7   DOC



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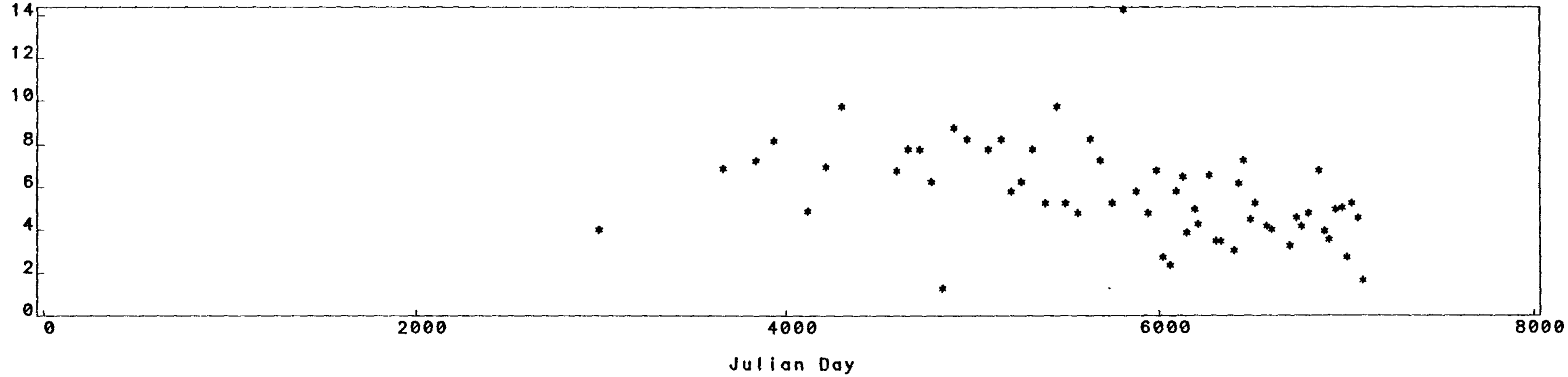

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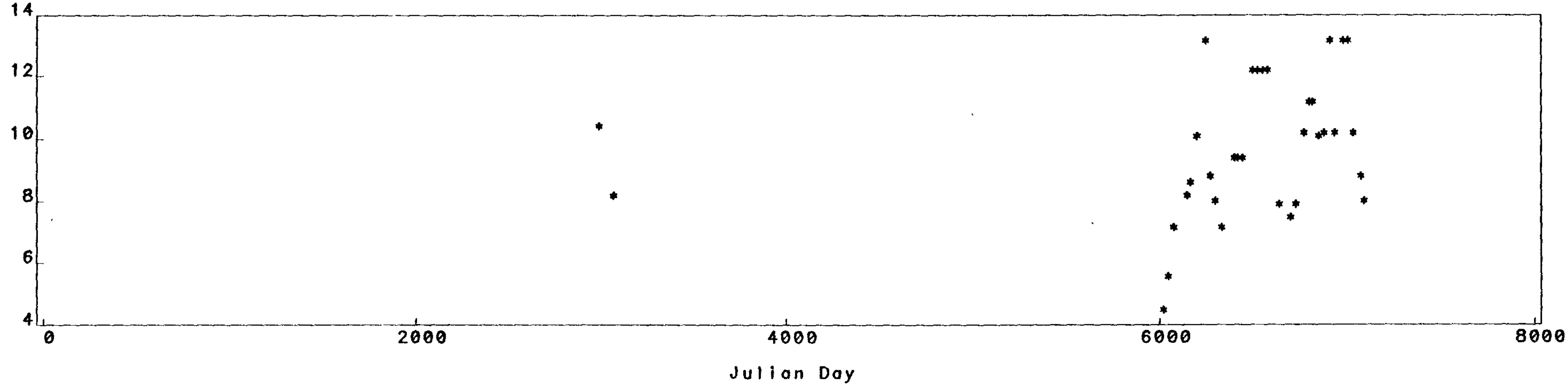

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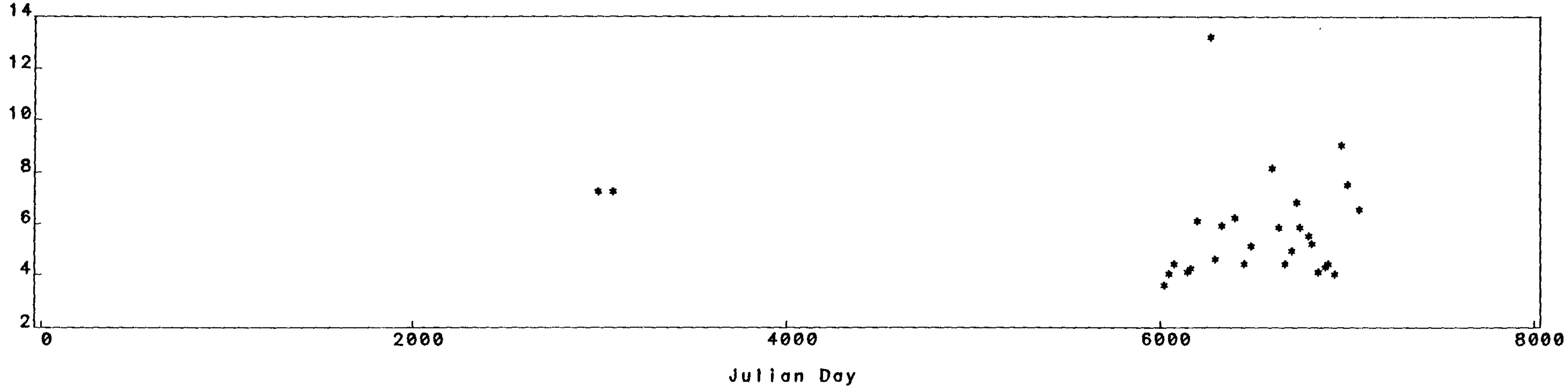

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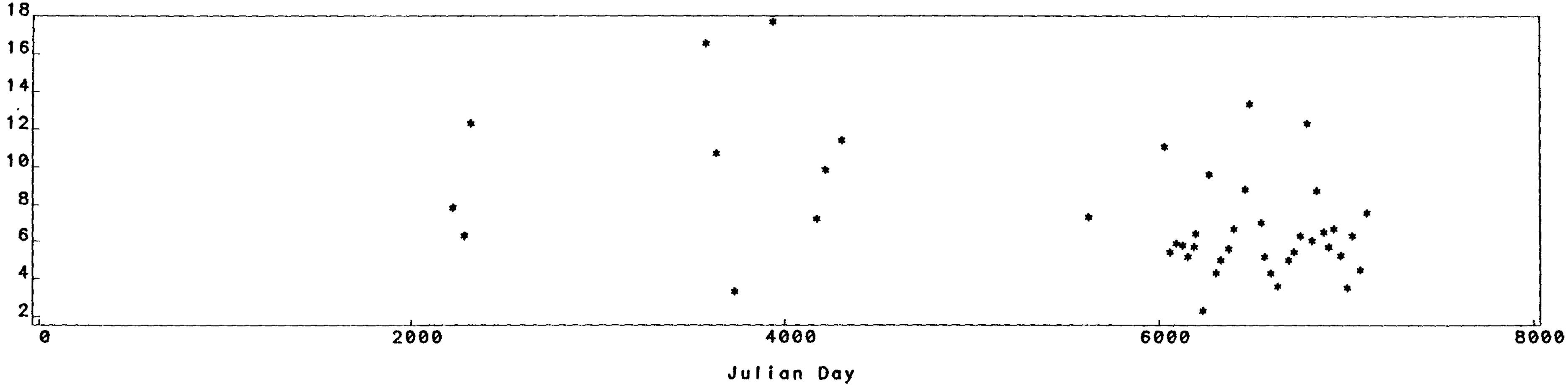

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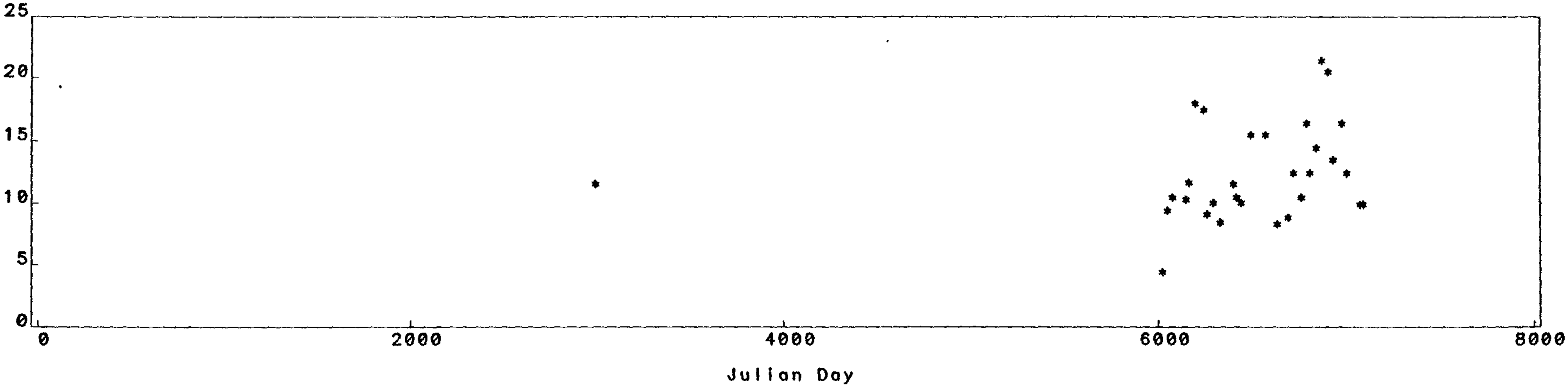

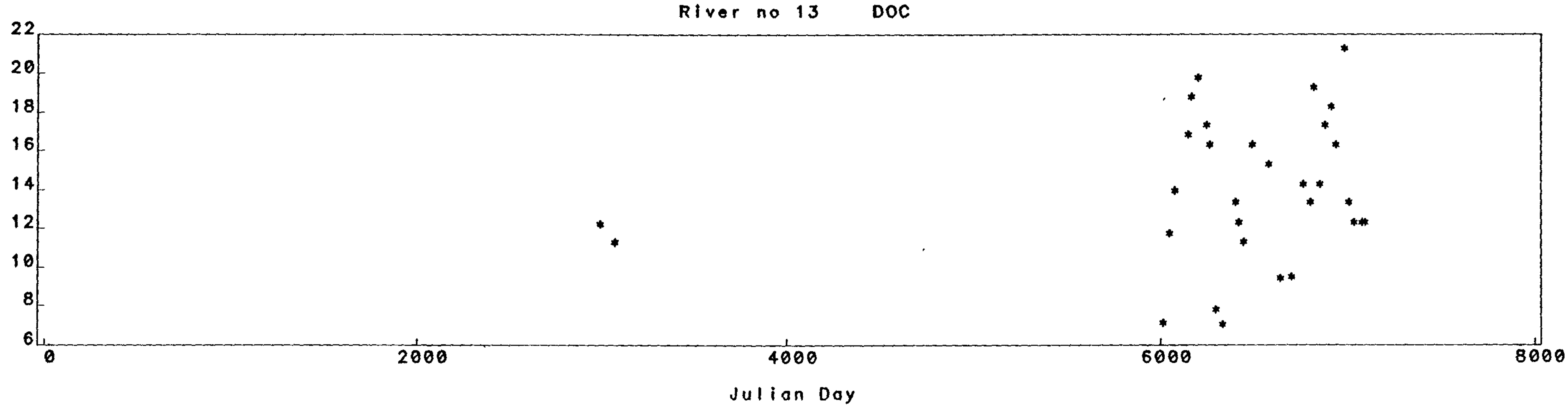
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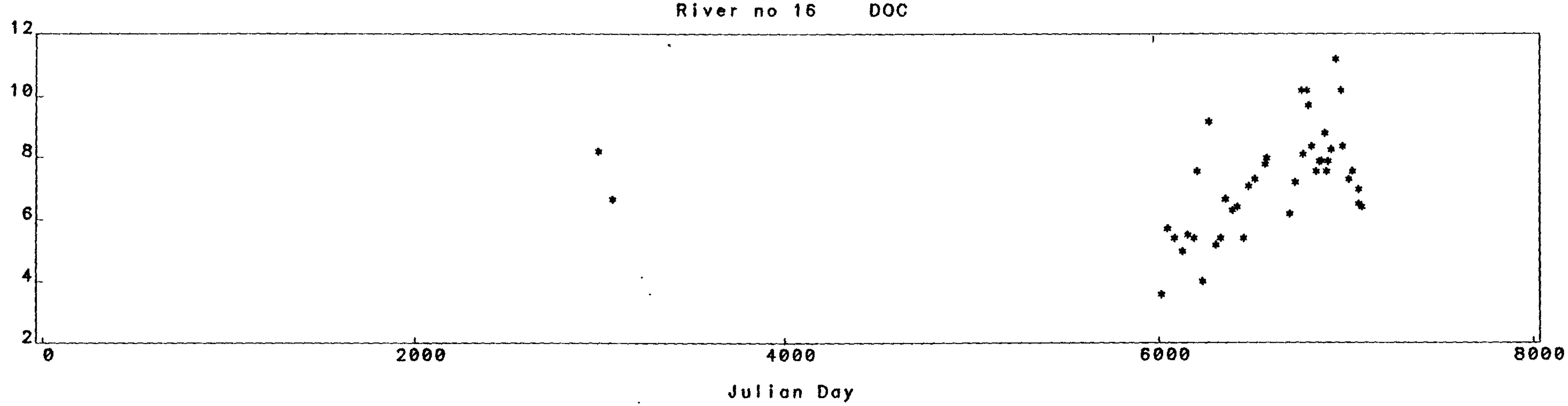
Julian Day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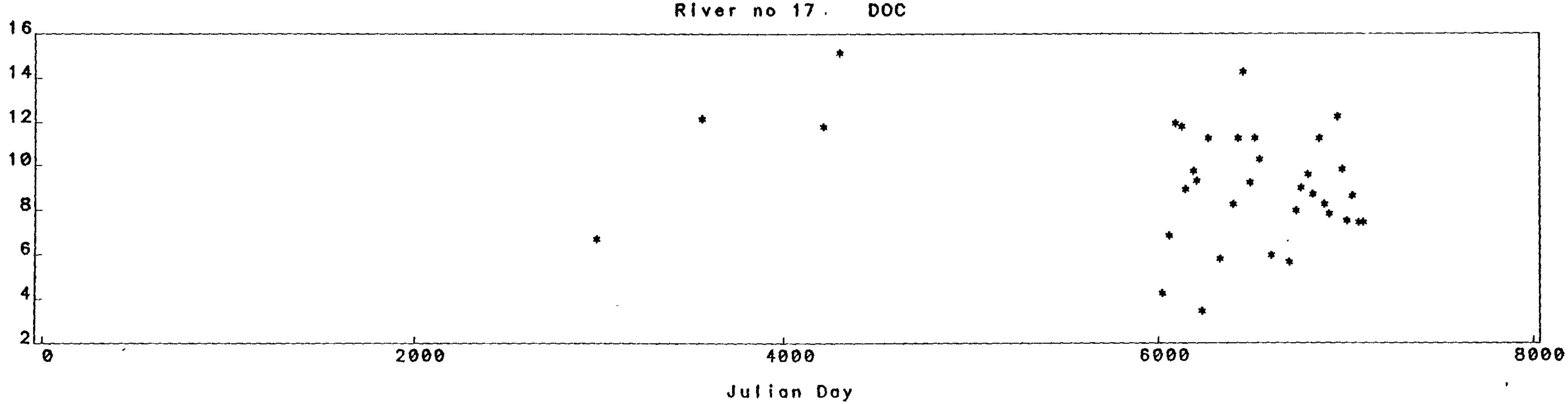
Julian Day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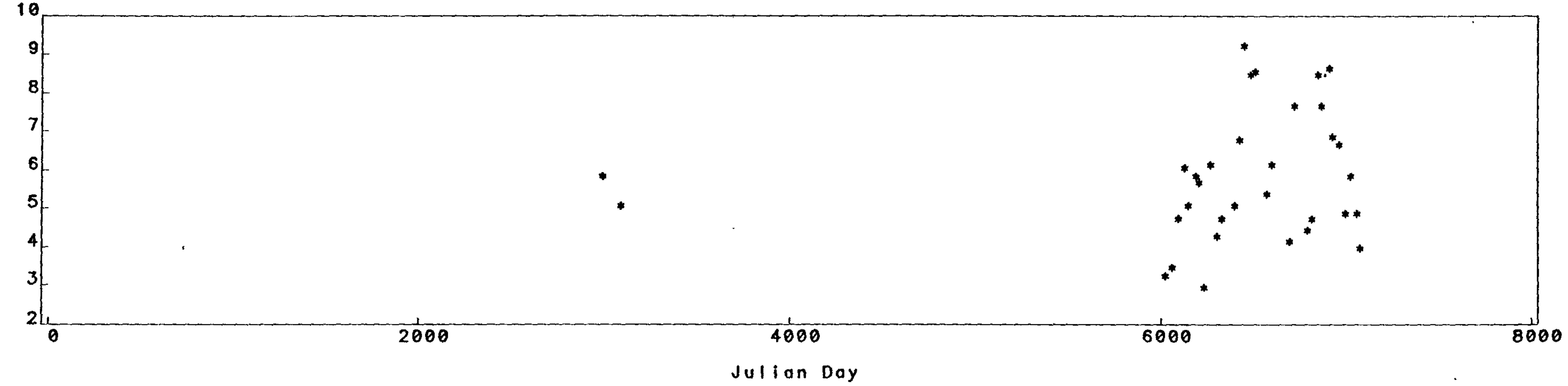
Julian Day

River no 18 DOC



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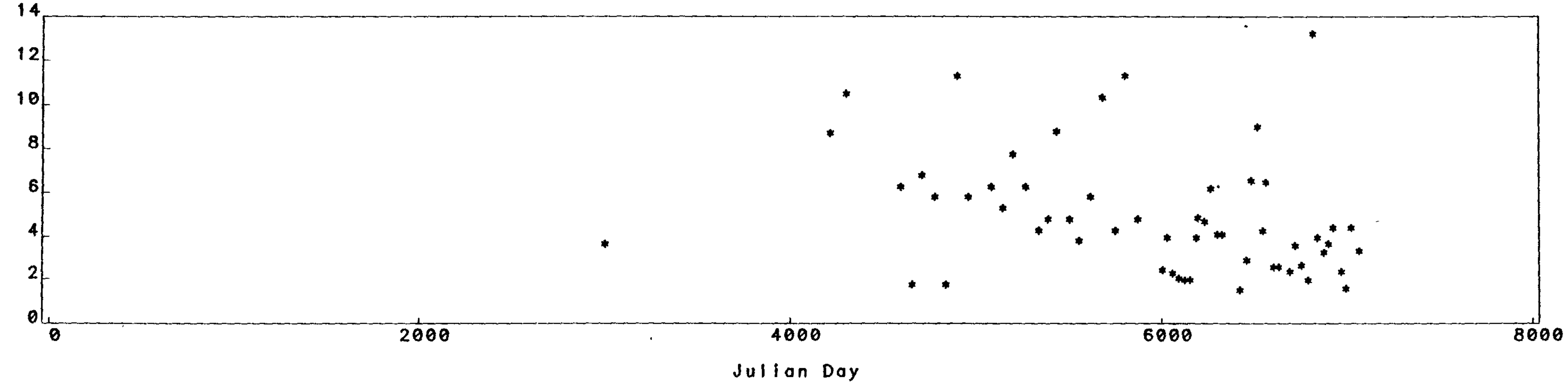

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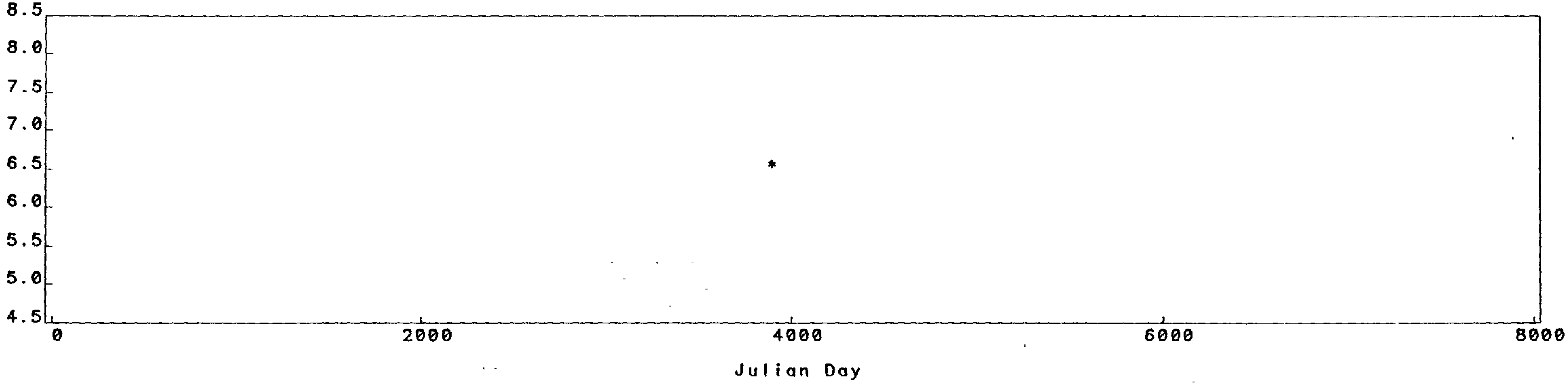

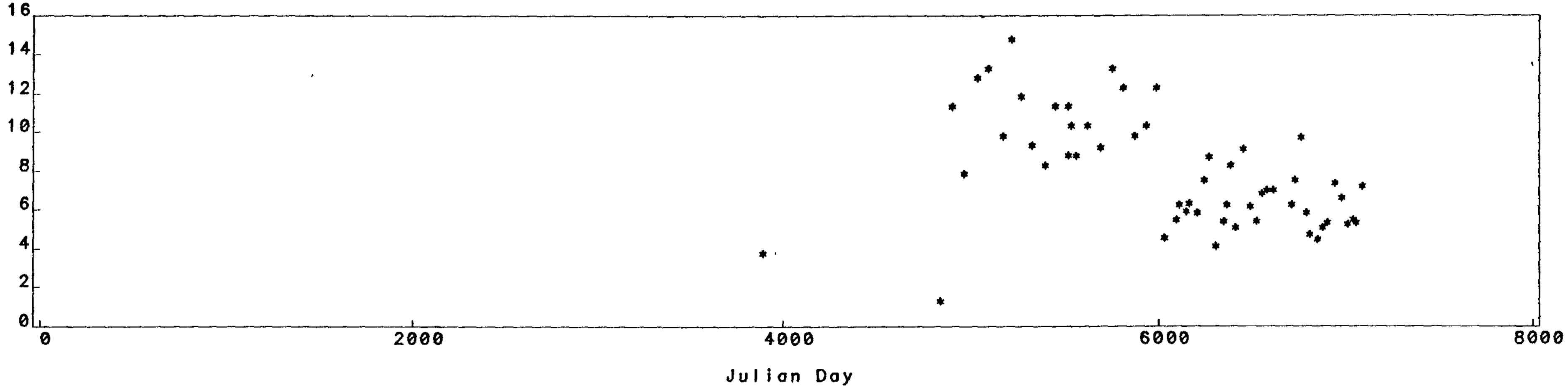

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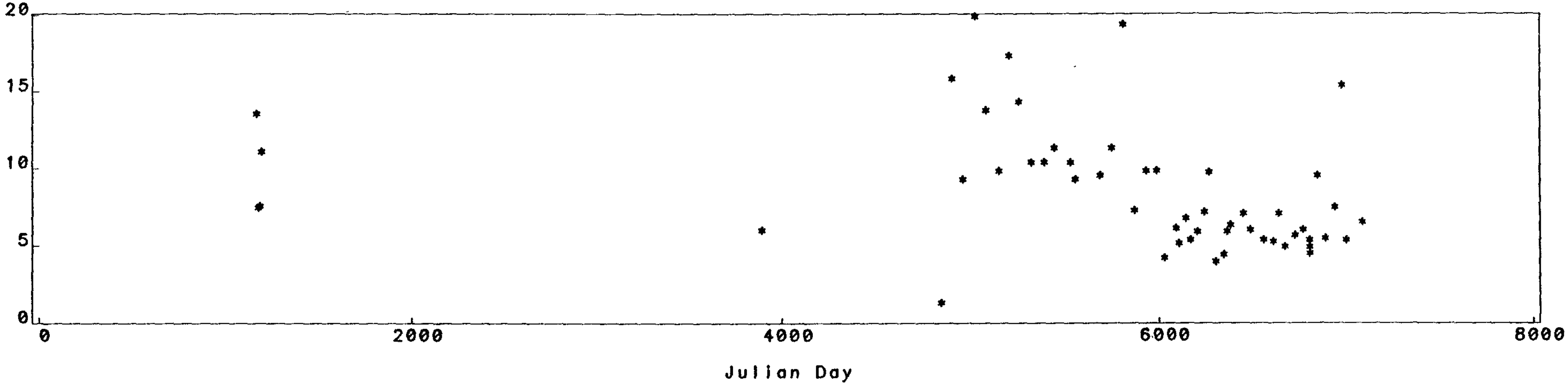

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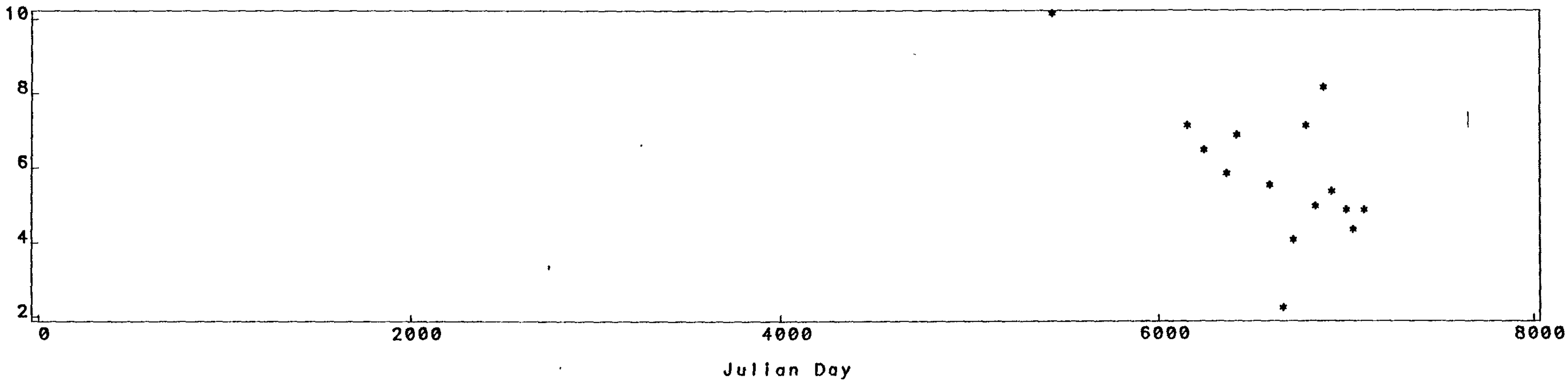

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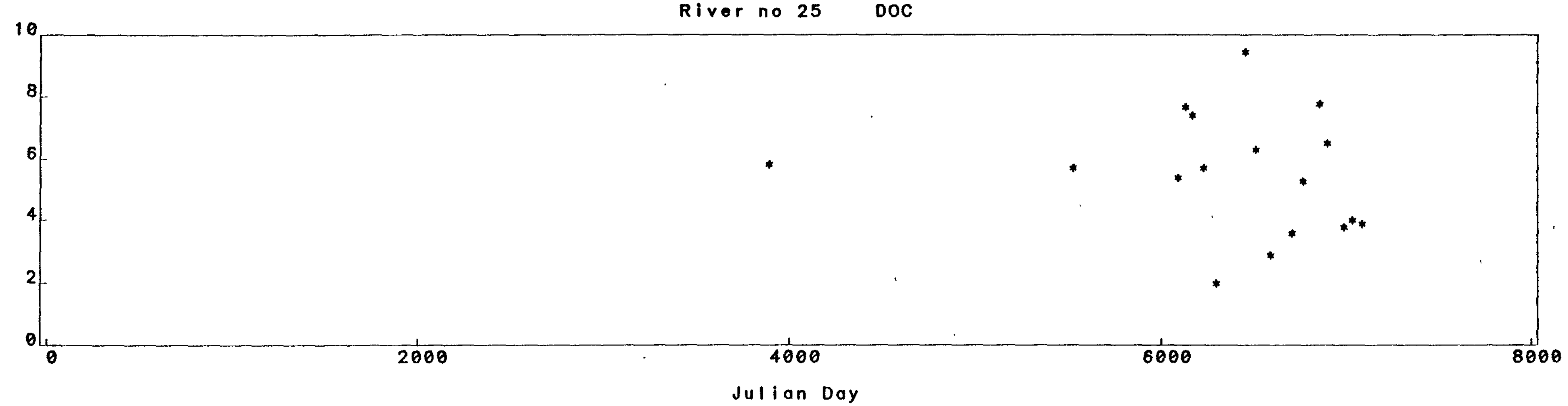
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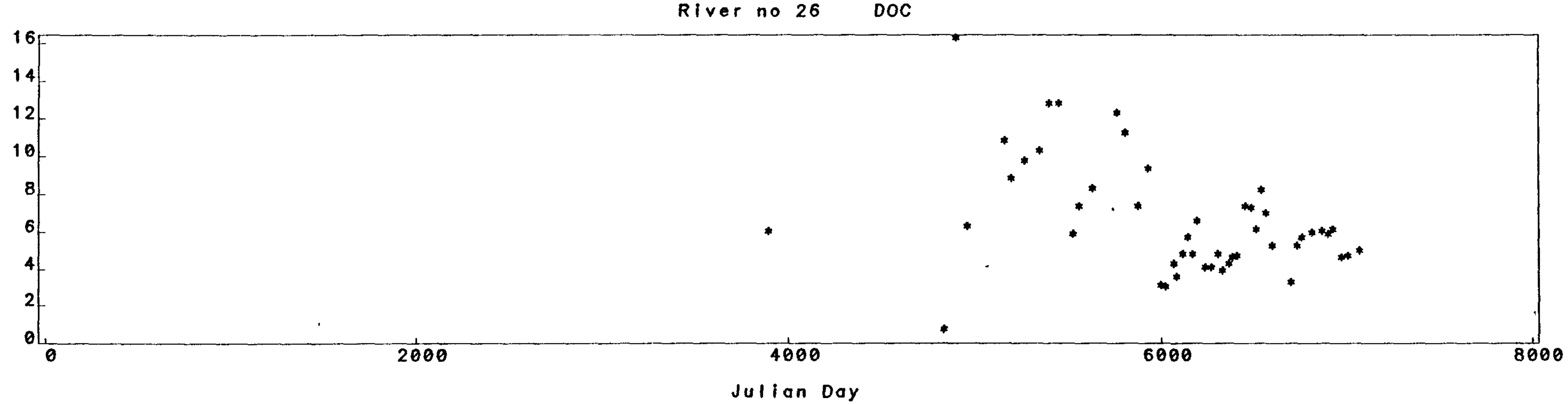
Julian Day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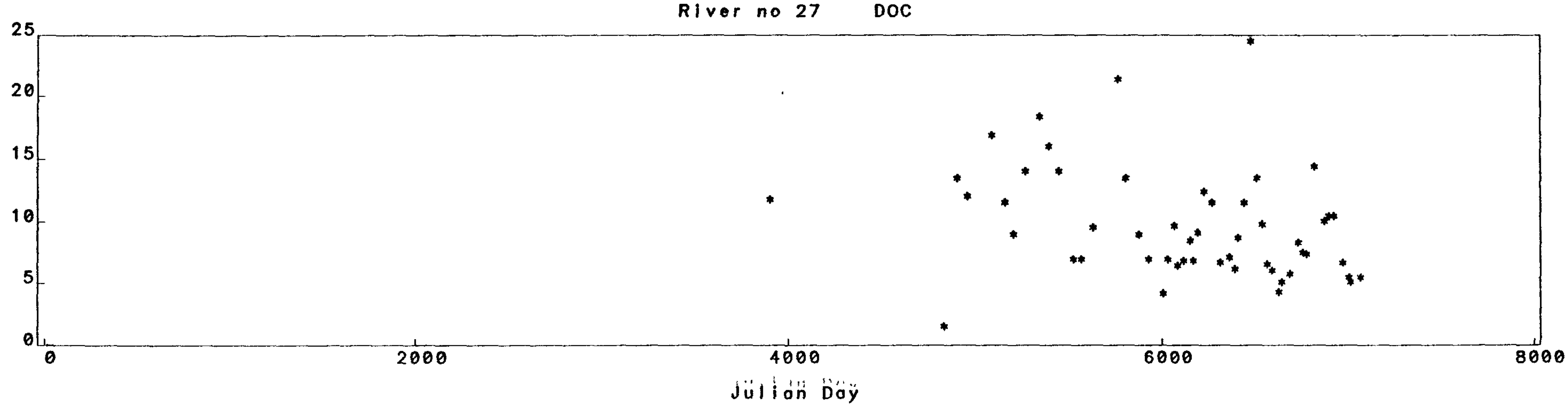
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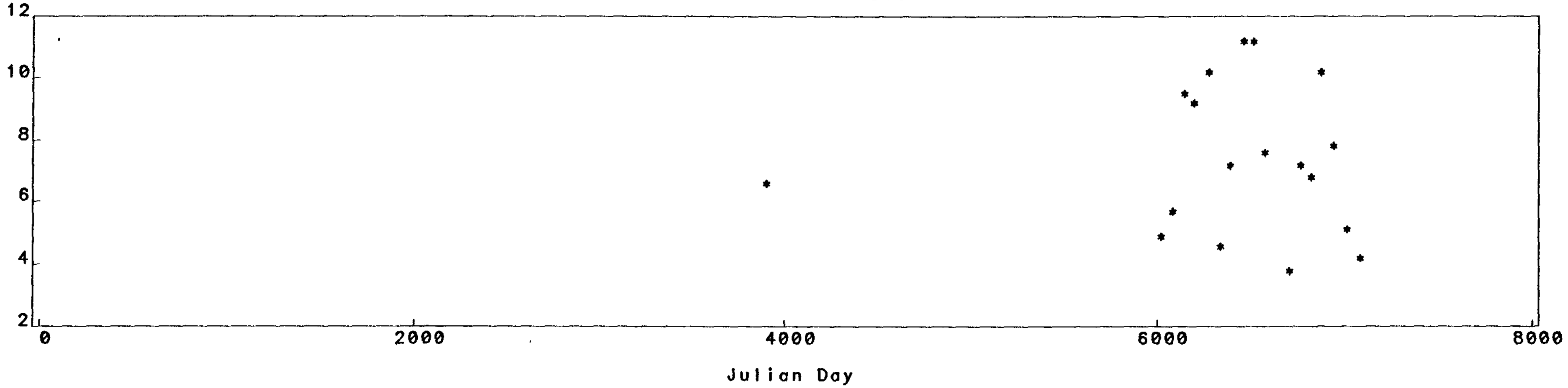
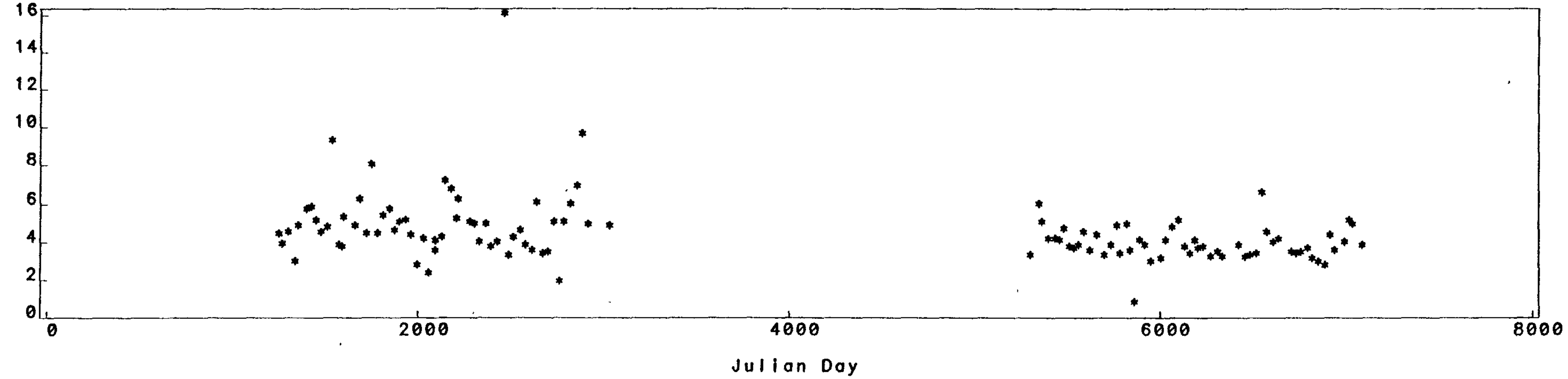
Julian Day



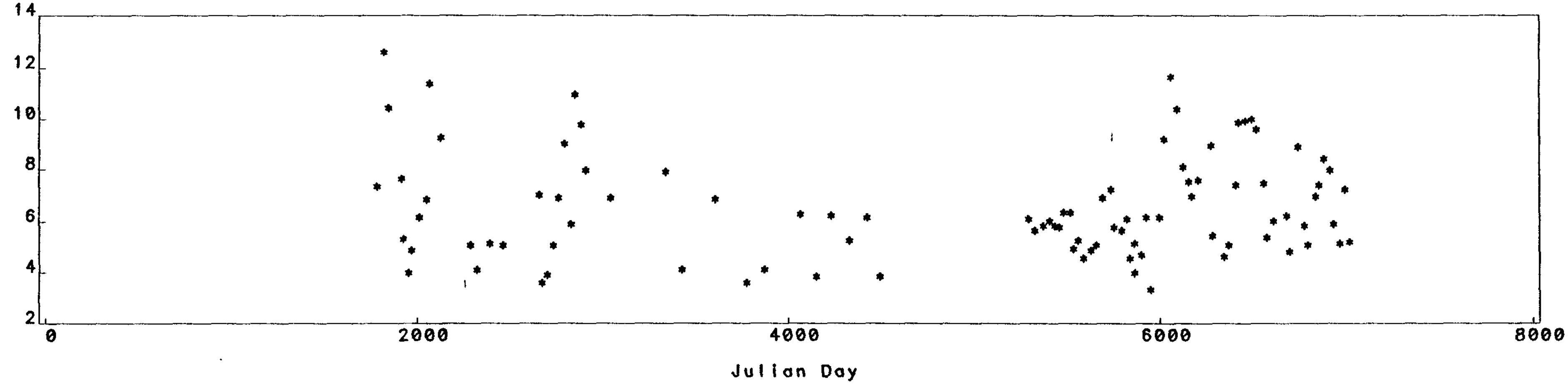
River no 28 DOC

Figure 5. Scatter plots of excess sulfate calculated by chloride ratio for the study rivers.

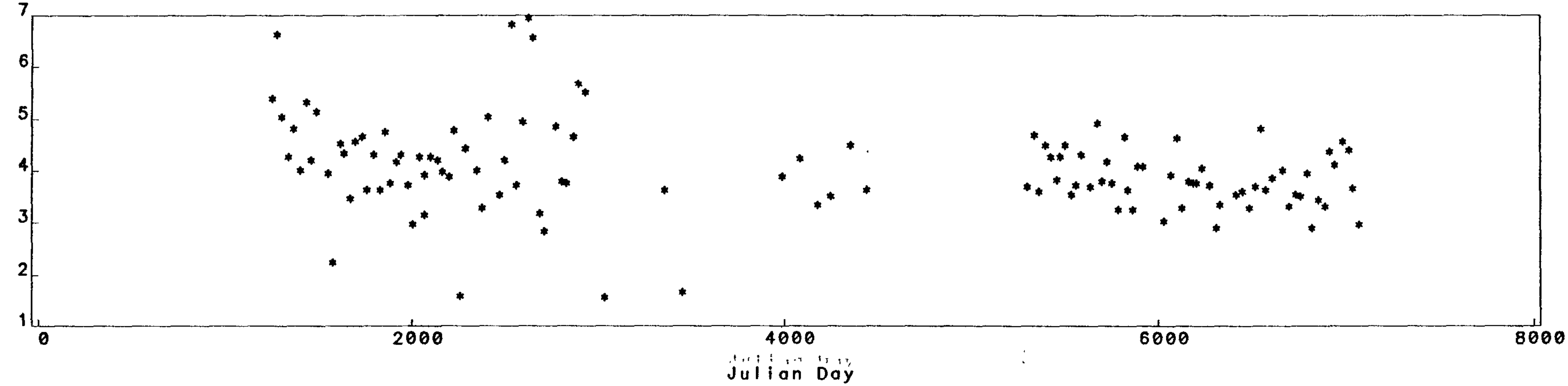
River no 1   Excess SO4 Cl

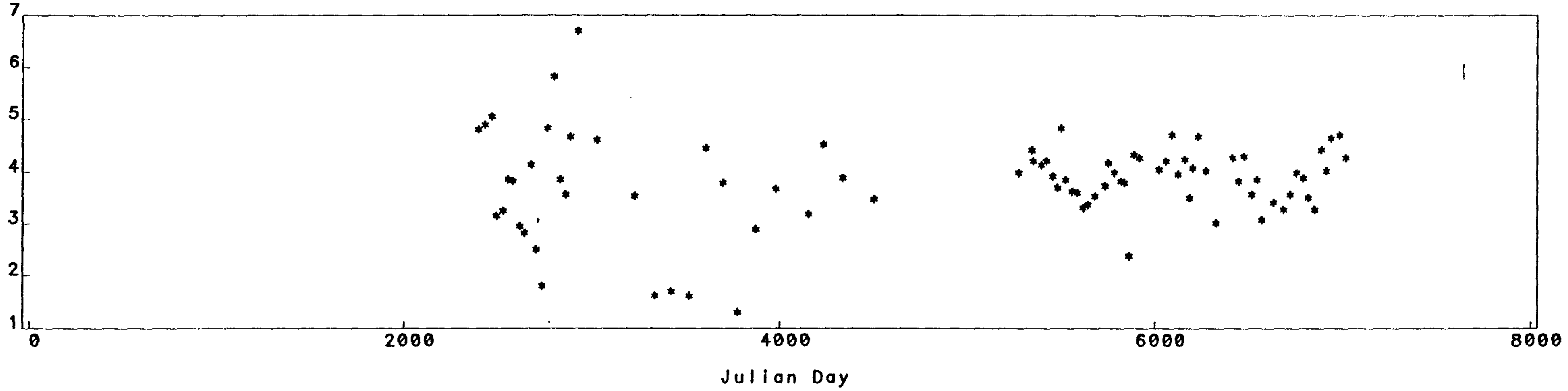


River no 2   Excess SO4 Cl

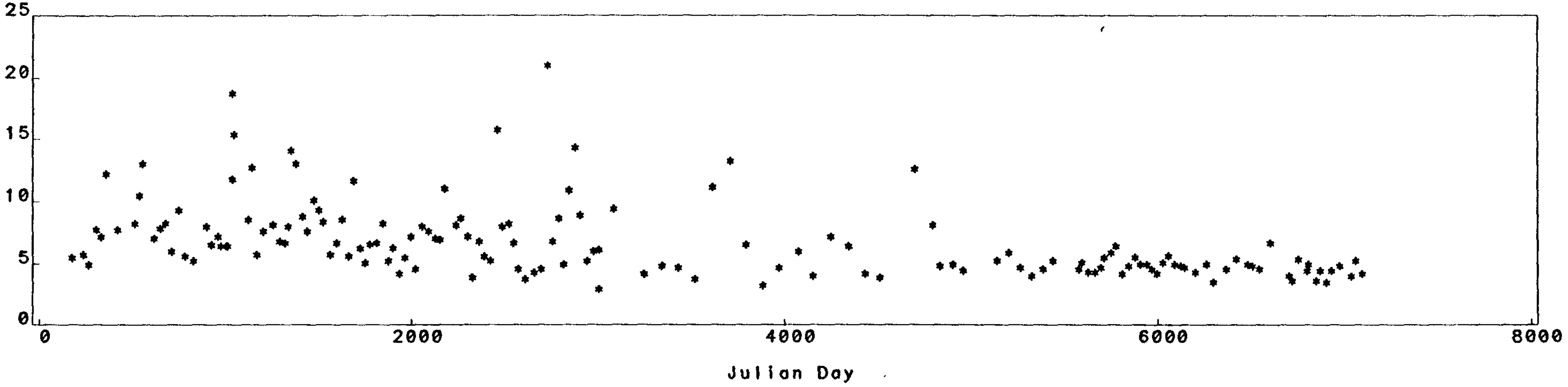


River no 3   Excess SO4 Cl





River no 4 Excess SO4 Cl



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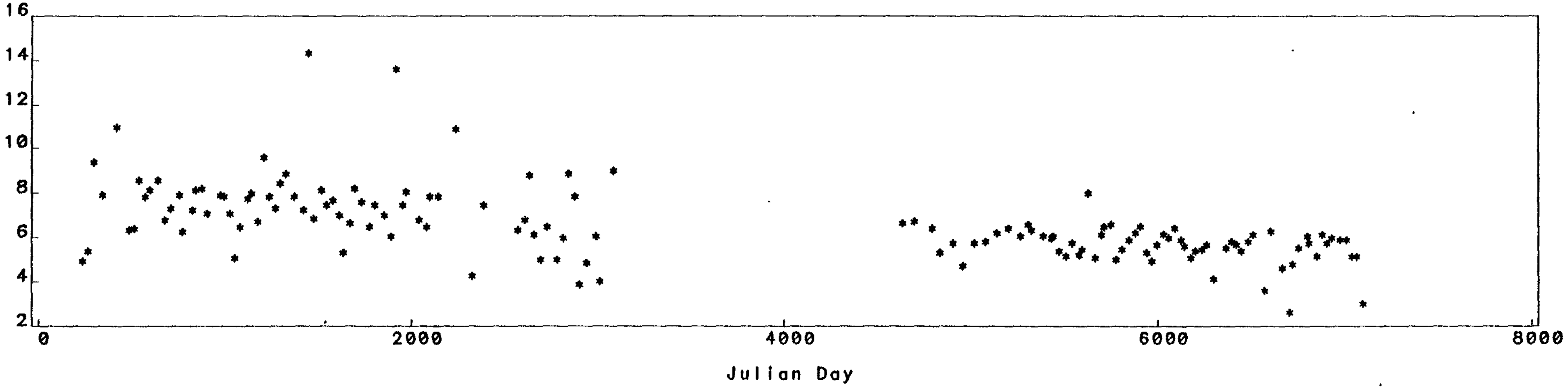
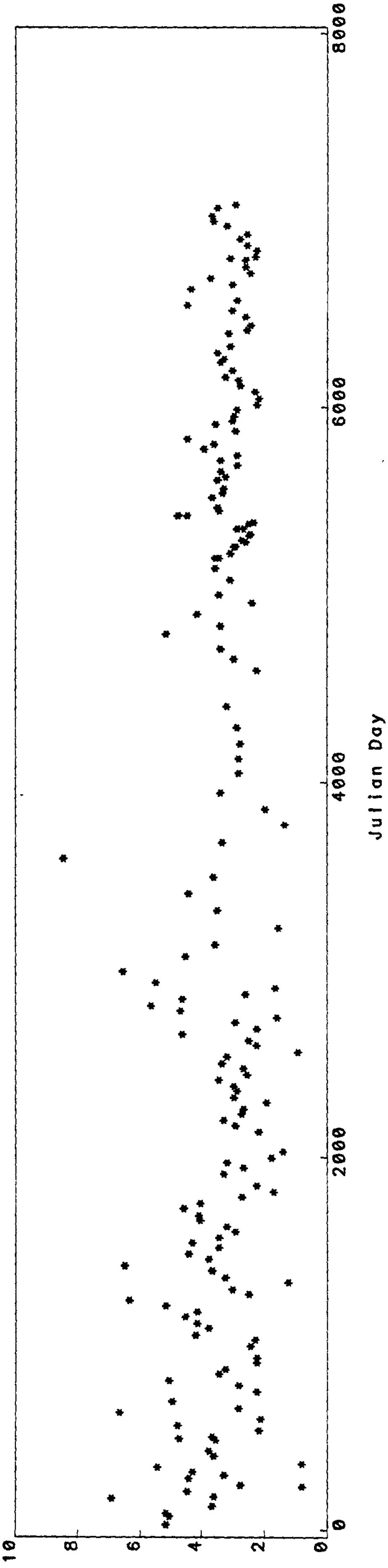
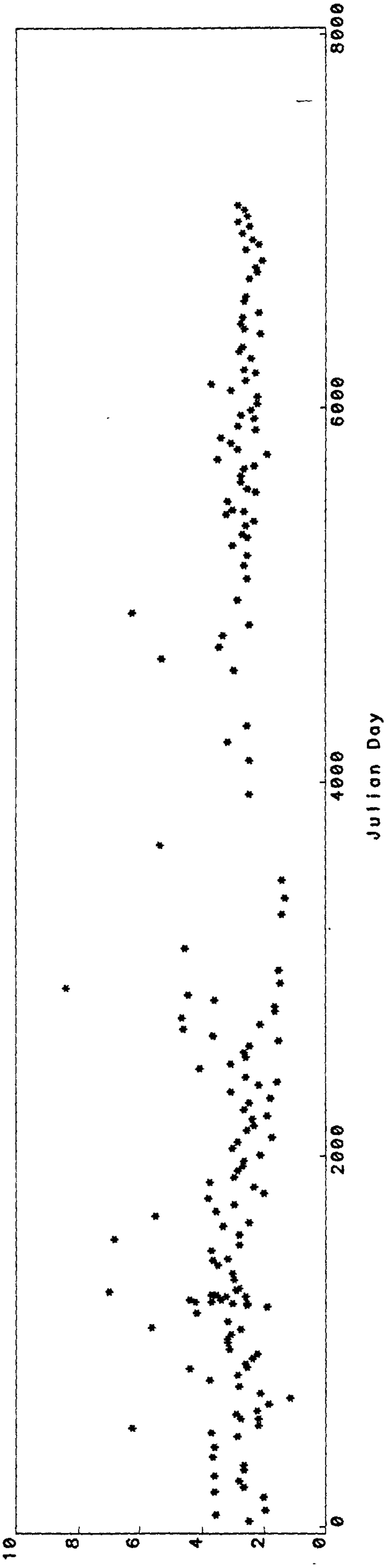


River no 6 Excess SO4 Cl

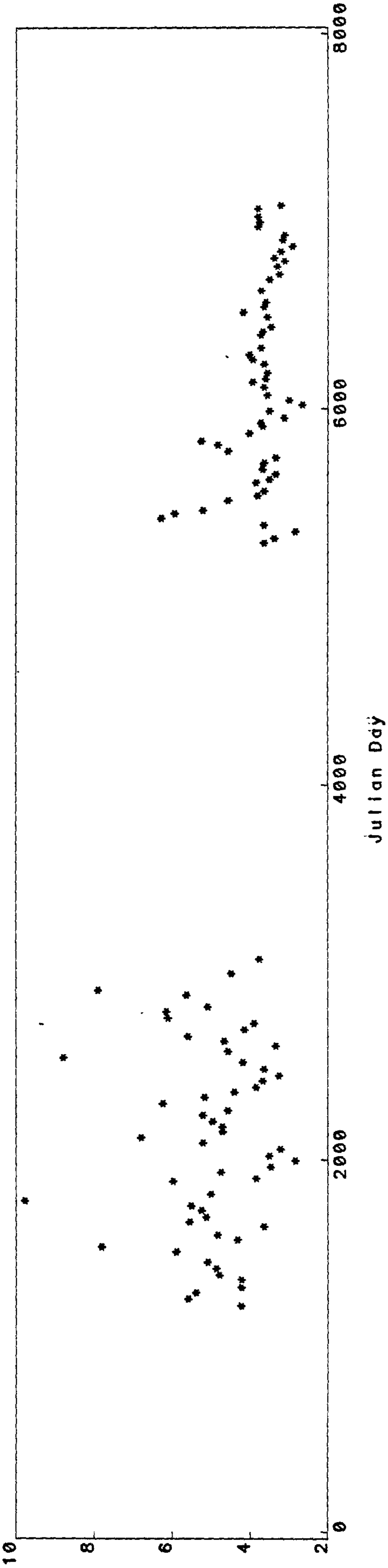
River no 7 Excess SO4 Cl

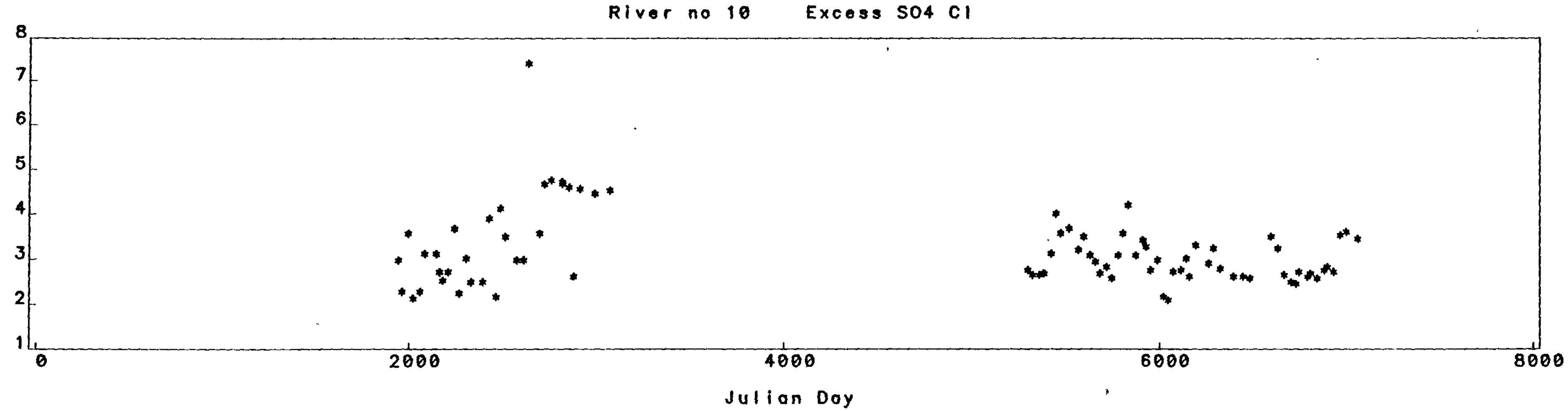


River no 8 Excess SO4 Cl



River no 9 Excess SO4 Cl

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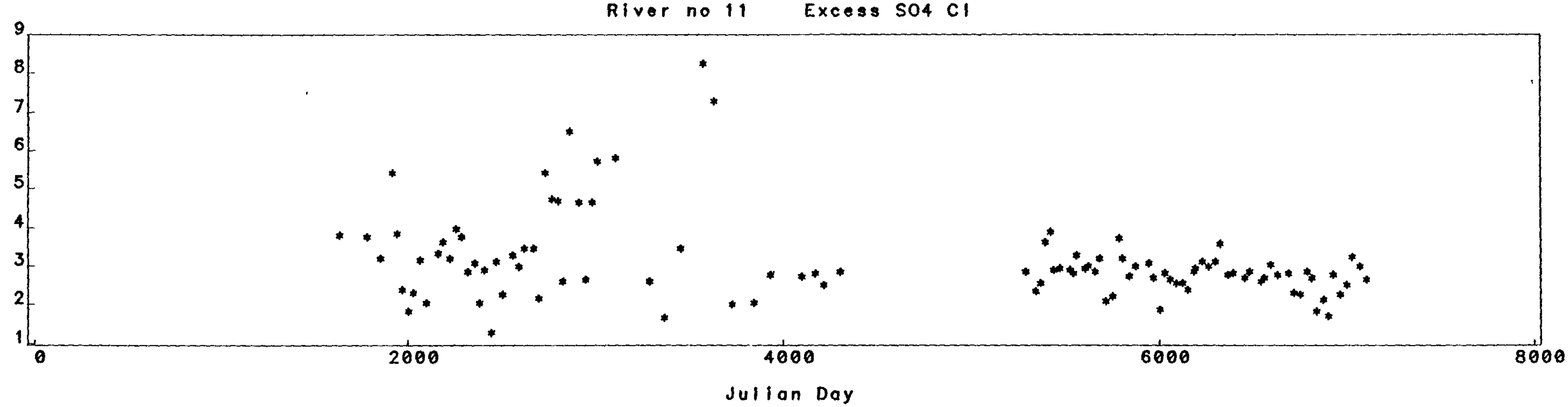
Julian Day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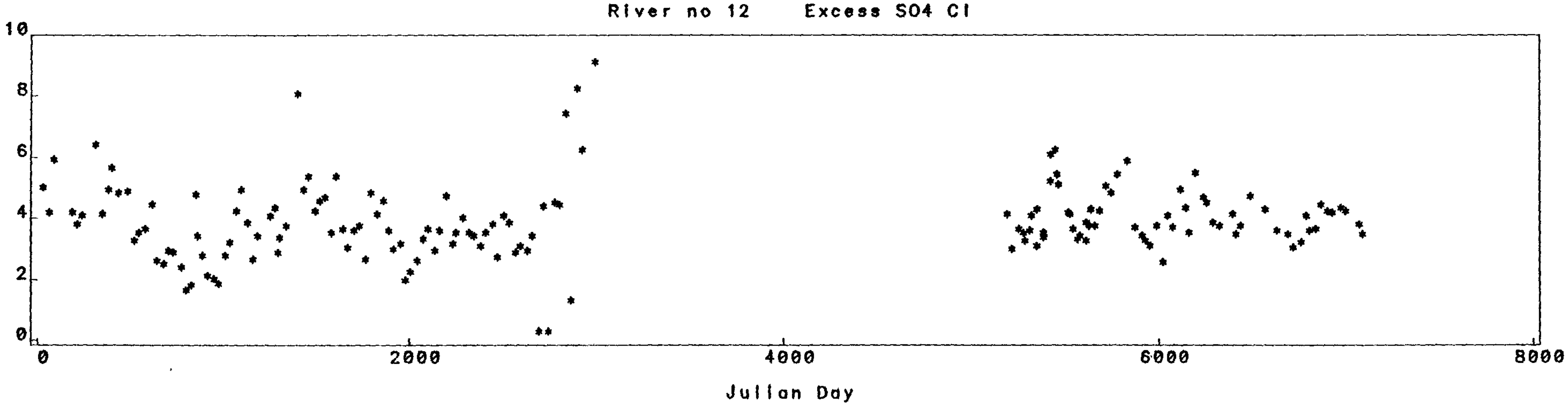
Julian Day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Julian Day

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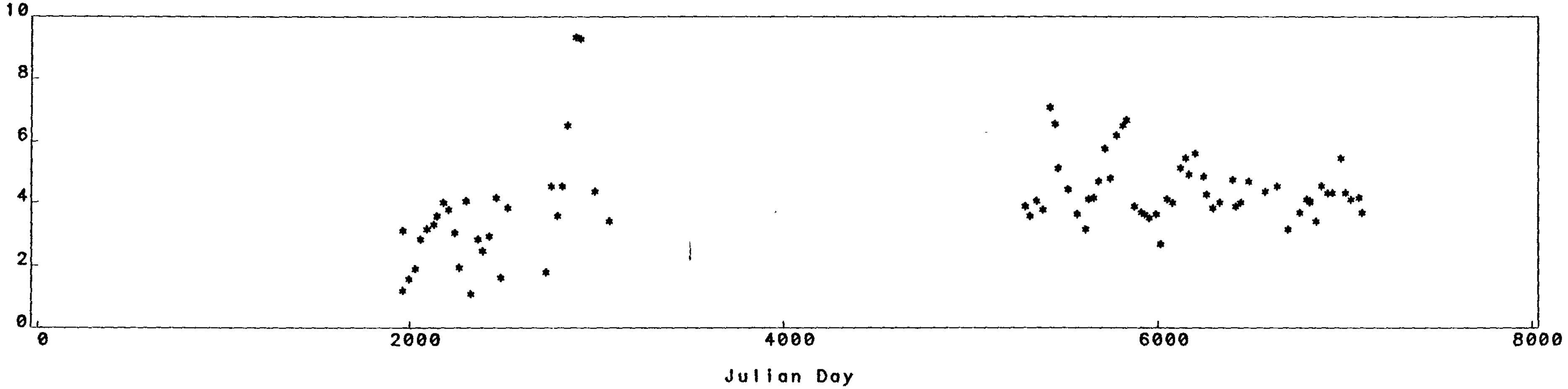

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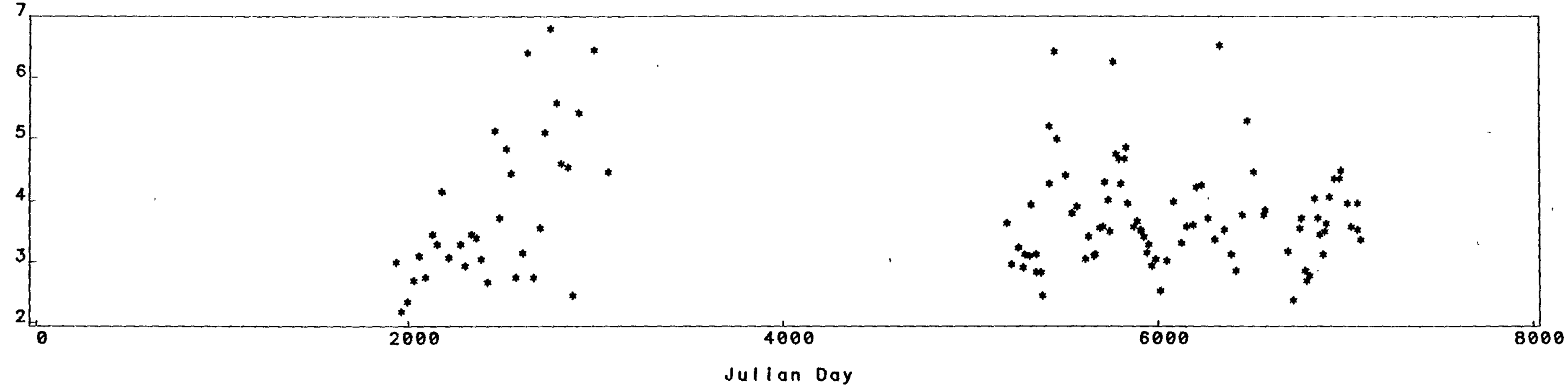

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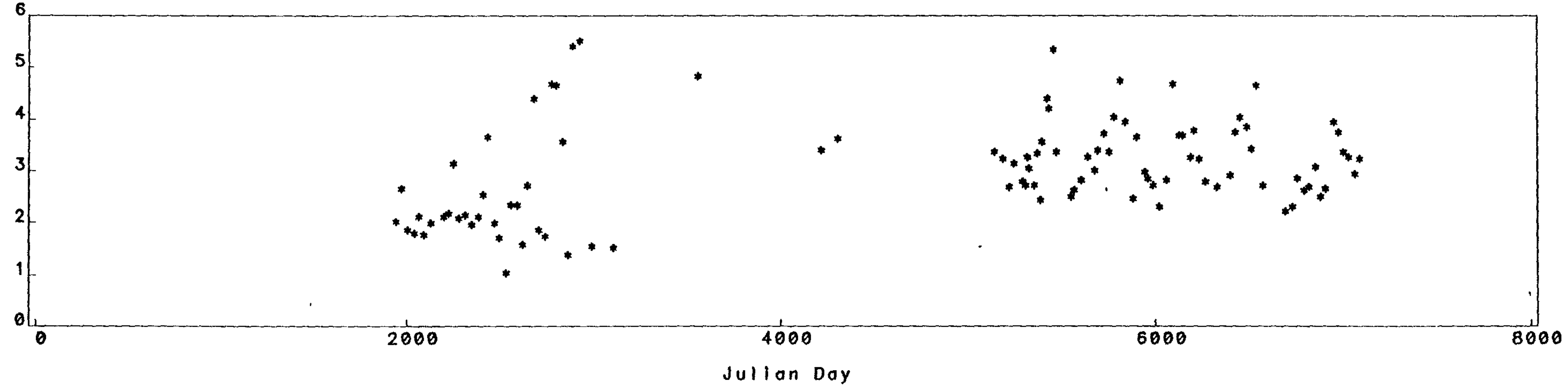

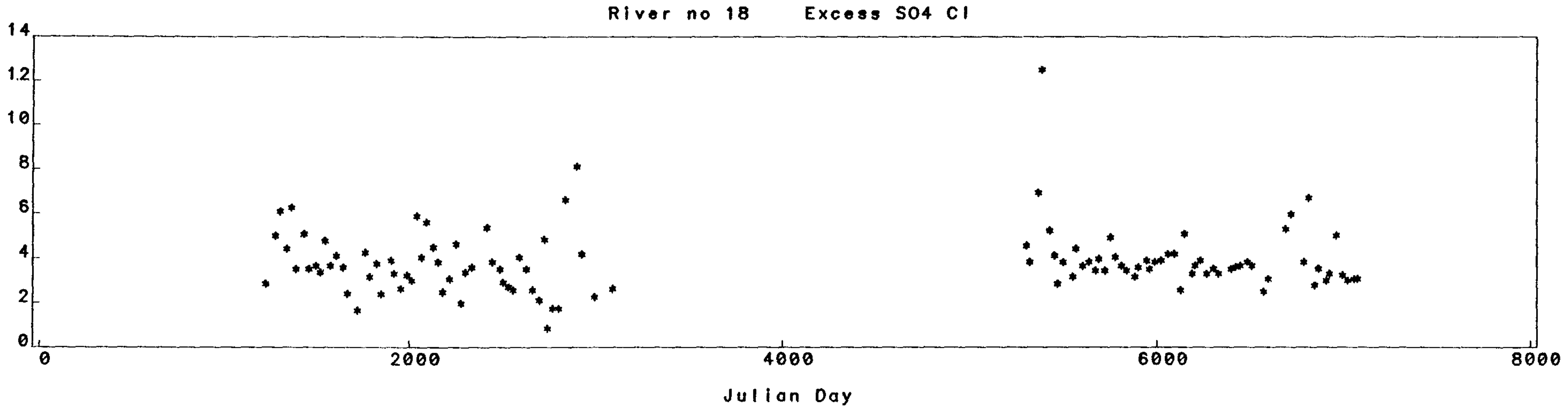
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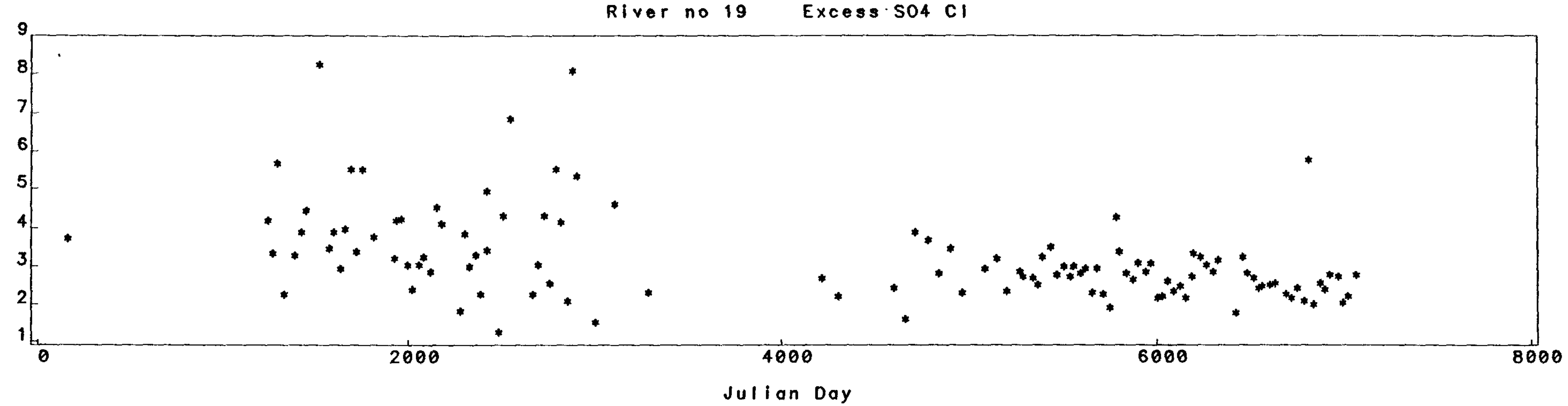
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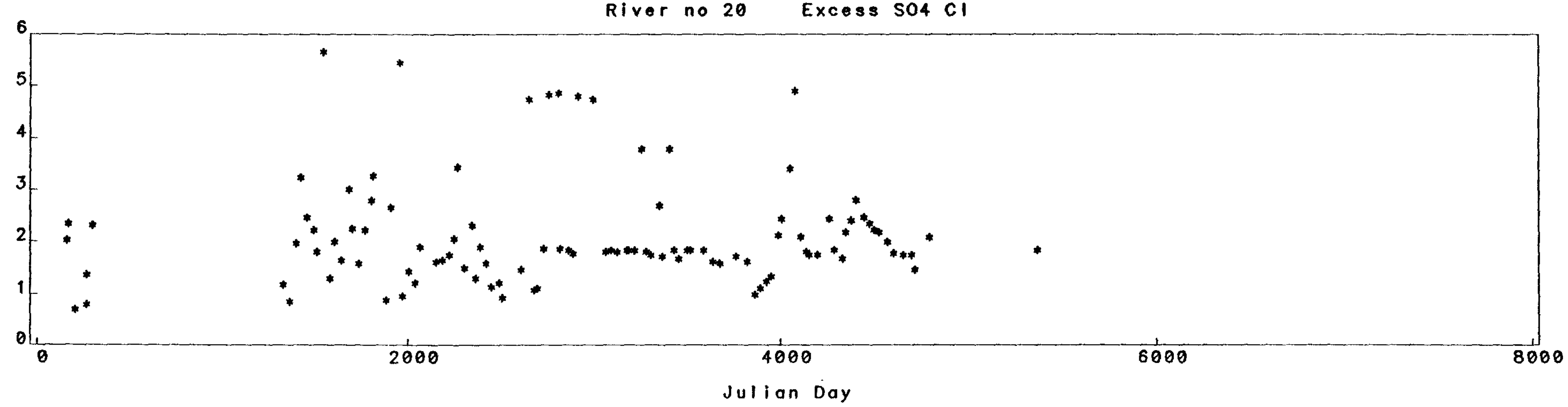
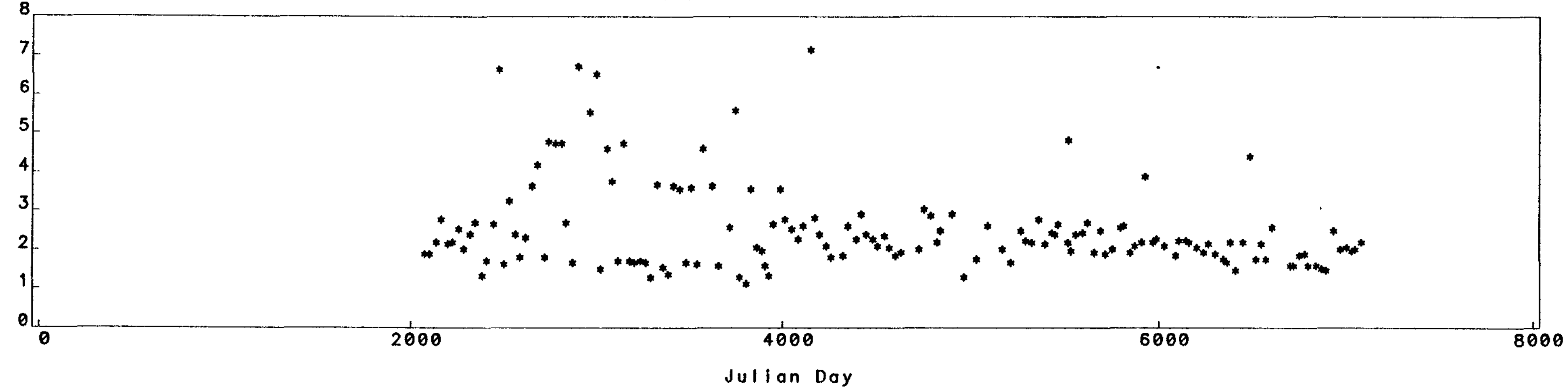
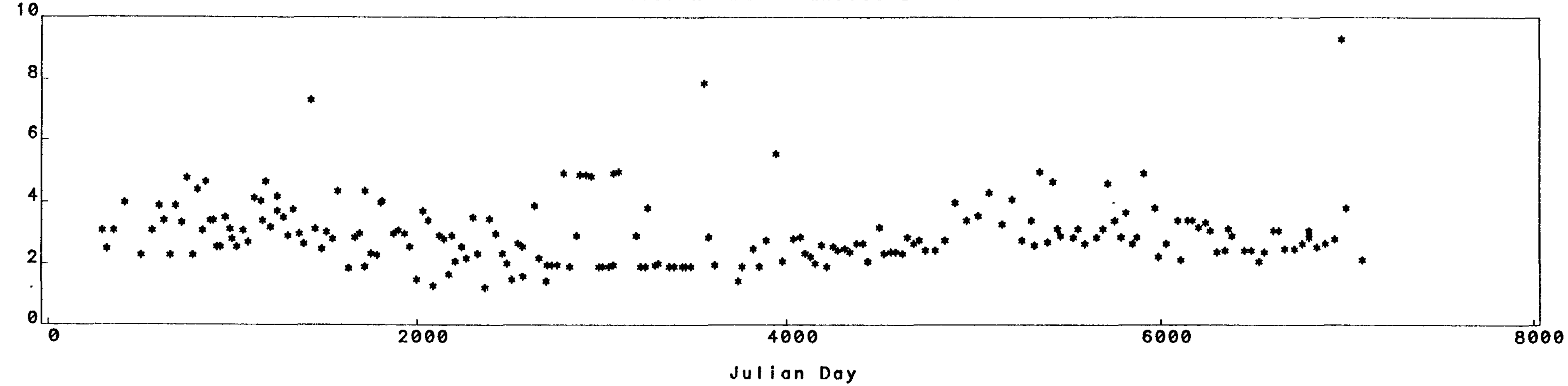
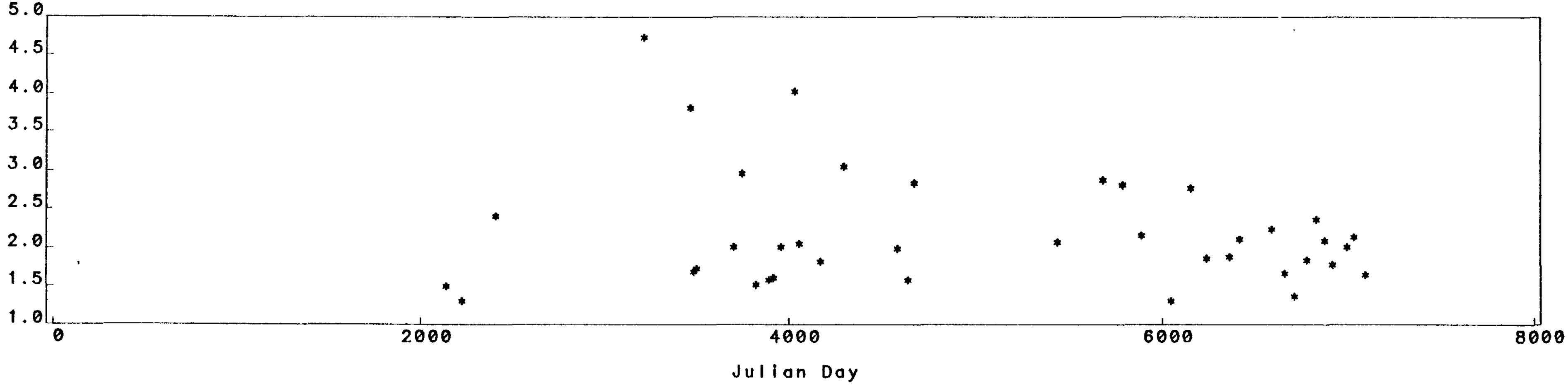

River no 20 Excess SO4 Cl



River no 21   Excess SO4 Cl

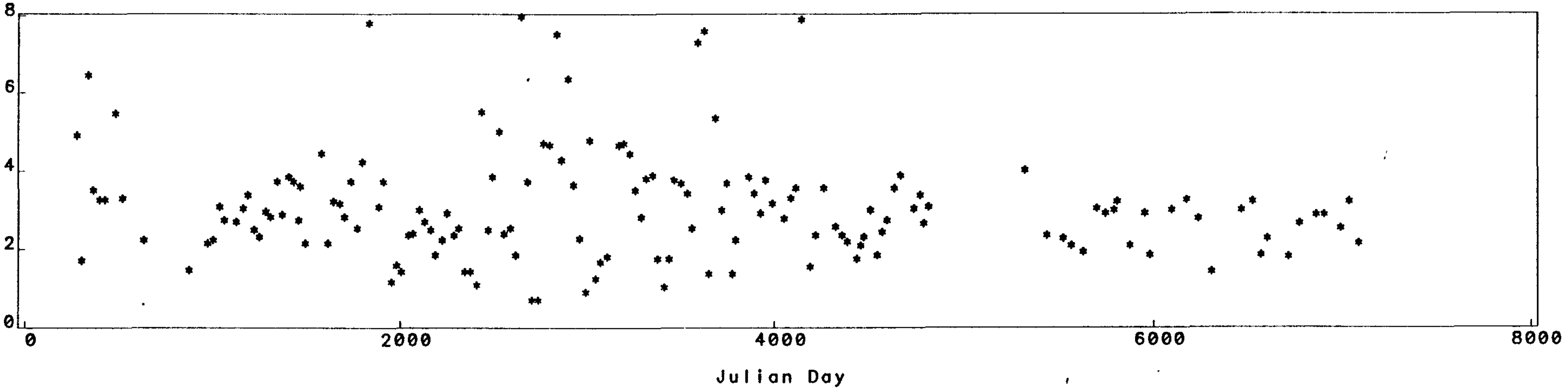


River no 22   Excess SO4 Cl

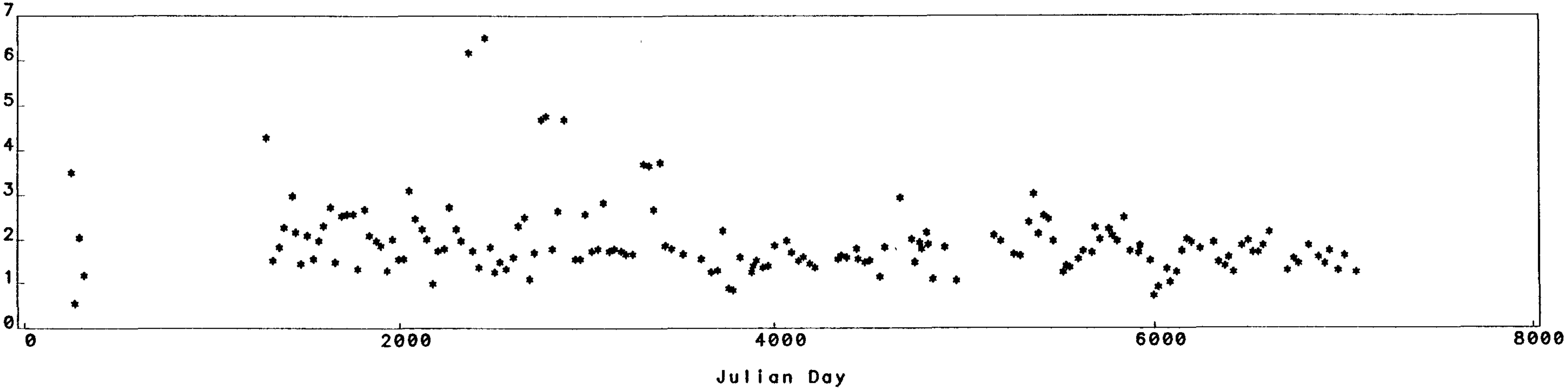


River no 23   Excess SO4 Cl

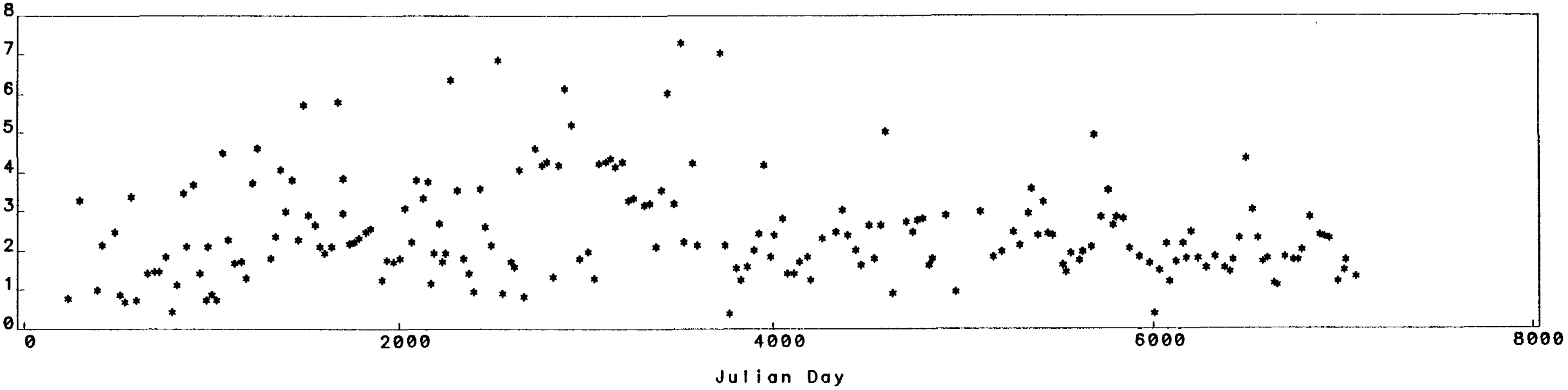
River no 25 Excess SO4 Cl



River no 26 Excess SO4 Cl



River no 27 Excess SO4 Cl



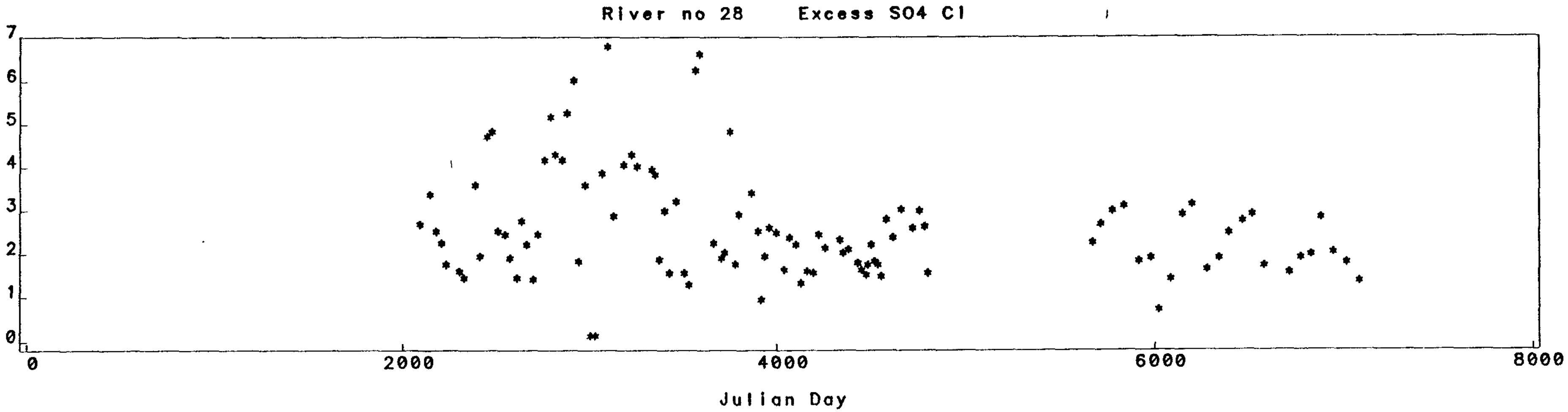
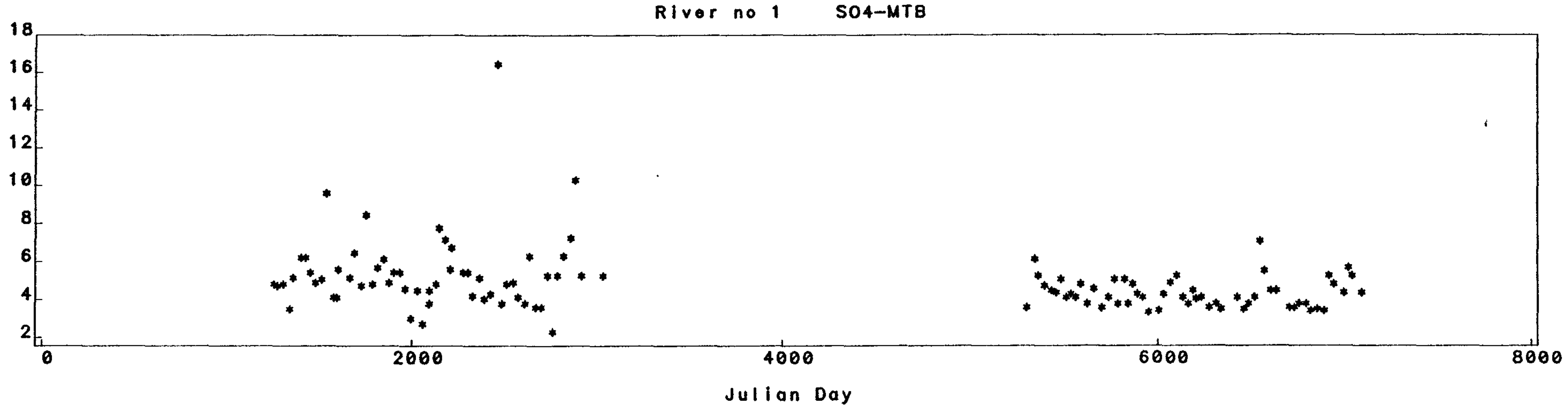
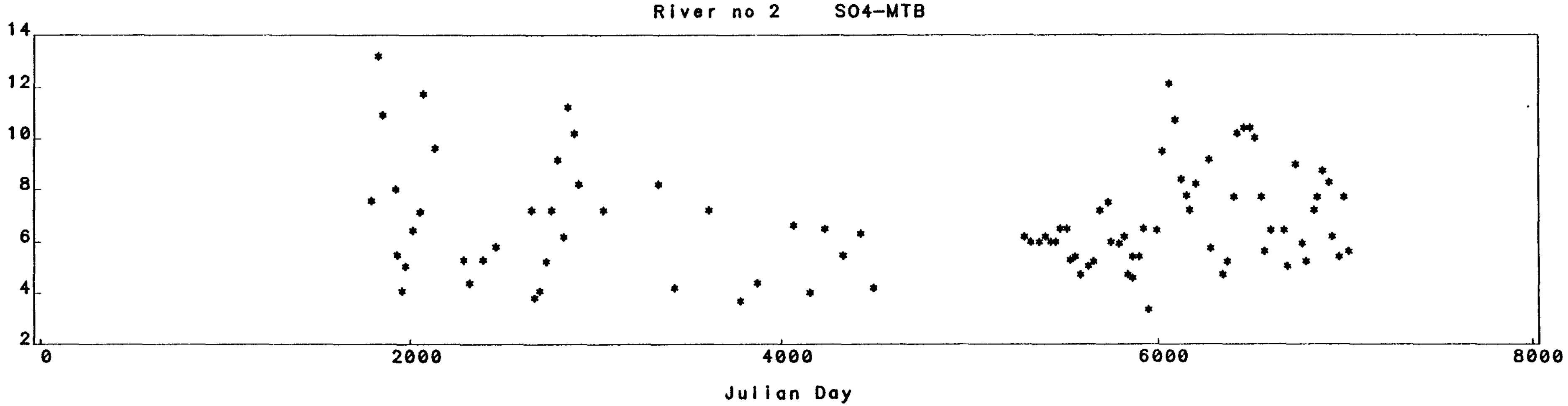
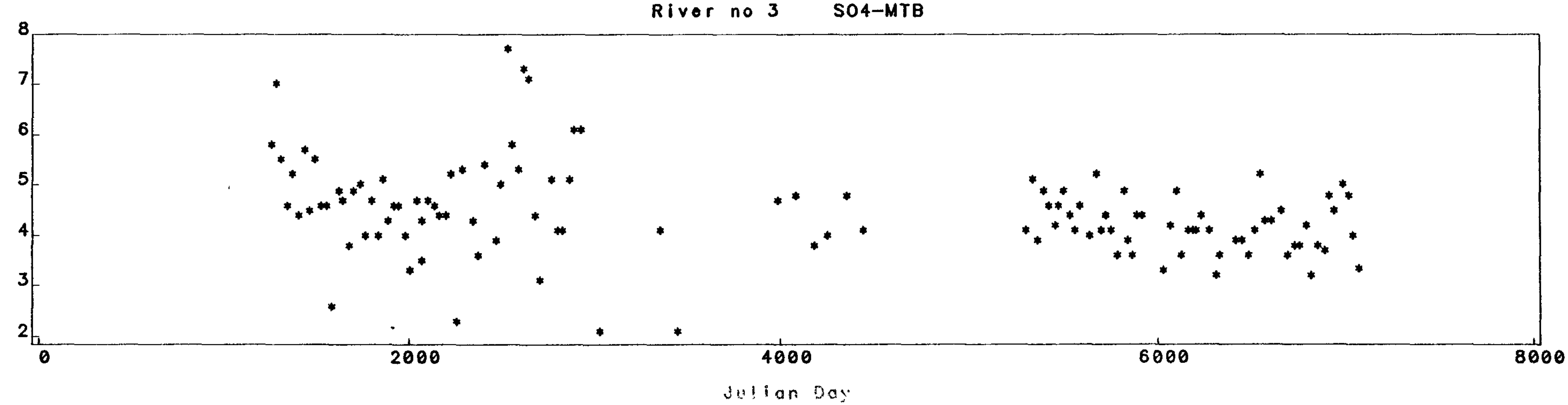
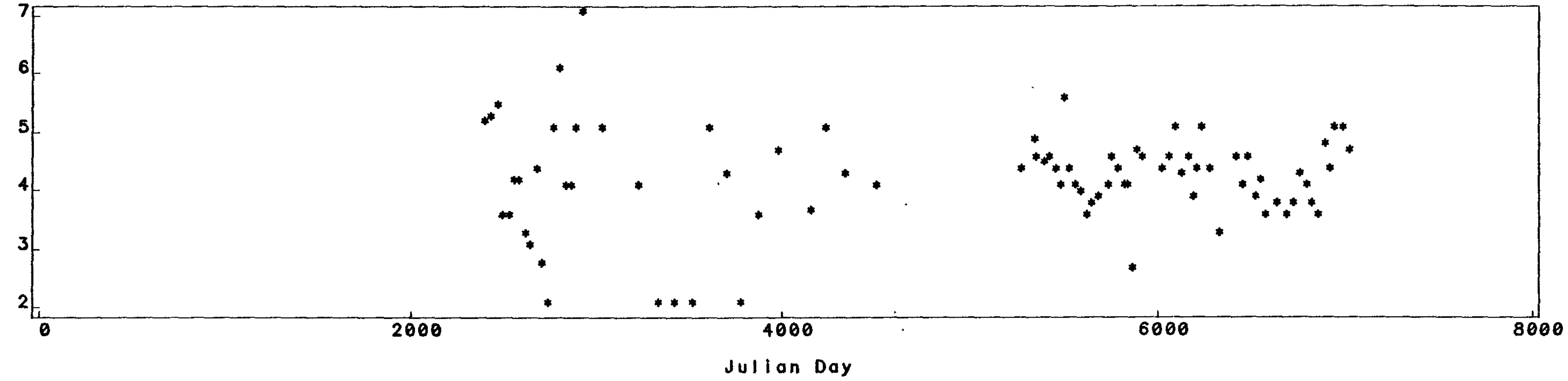

River no 28 Excess SO4 Cl
7
6
5
4
3
2
1
0
0
2000
4000
6000
8000
Julian Day

Figure 6. Scatter plots of sulfate-MTB for the study rivers.

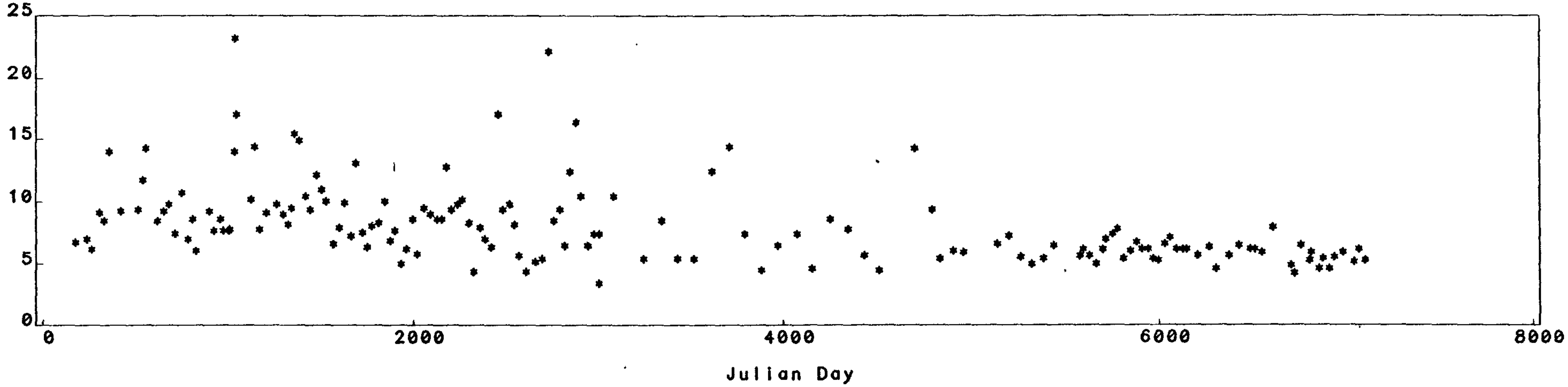

River no 1
SO4-MTB
18
16
14
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day


River no 2
SO4-MTB
14
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day

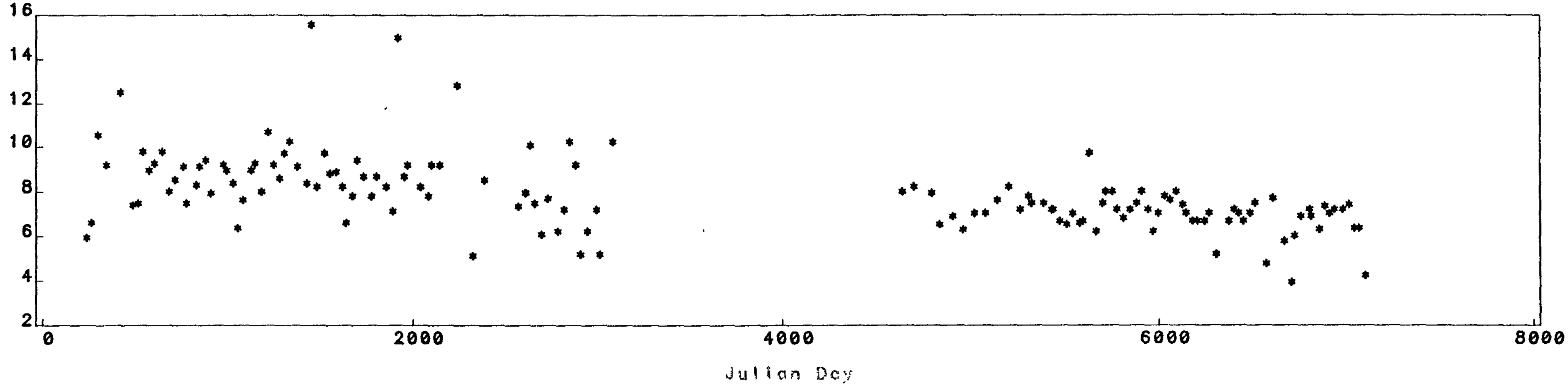

River no 3
SO4-MTB
8
7
6
5
4
3
2
0
2000
4000
6000
8000
Julian Day



River no 4 SO4-MTB

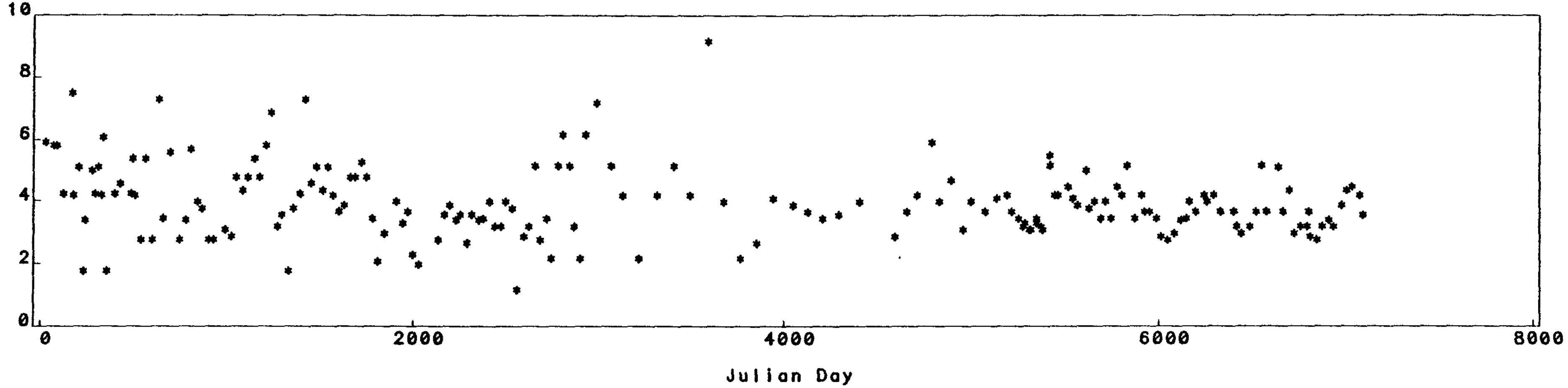


River no 5 SO4-MTB

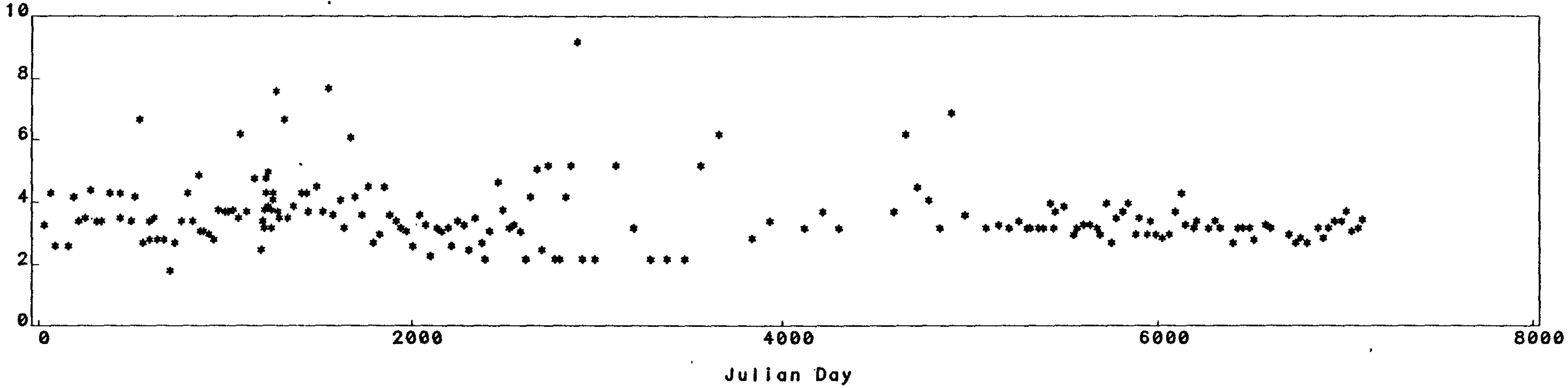


River no 6 SO4-MTB

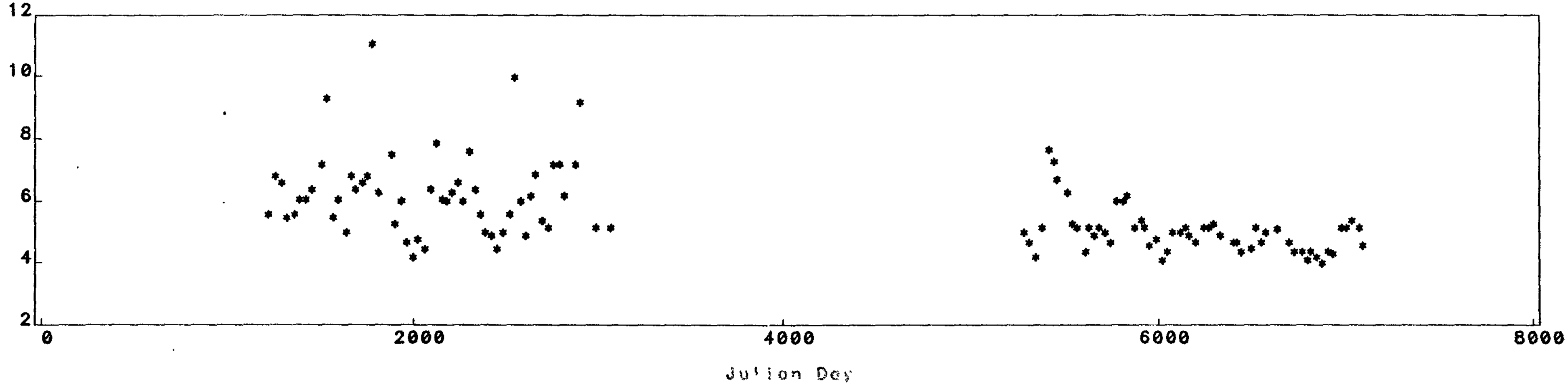
River no 7 SO4-MTB



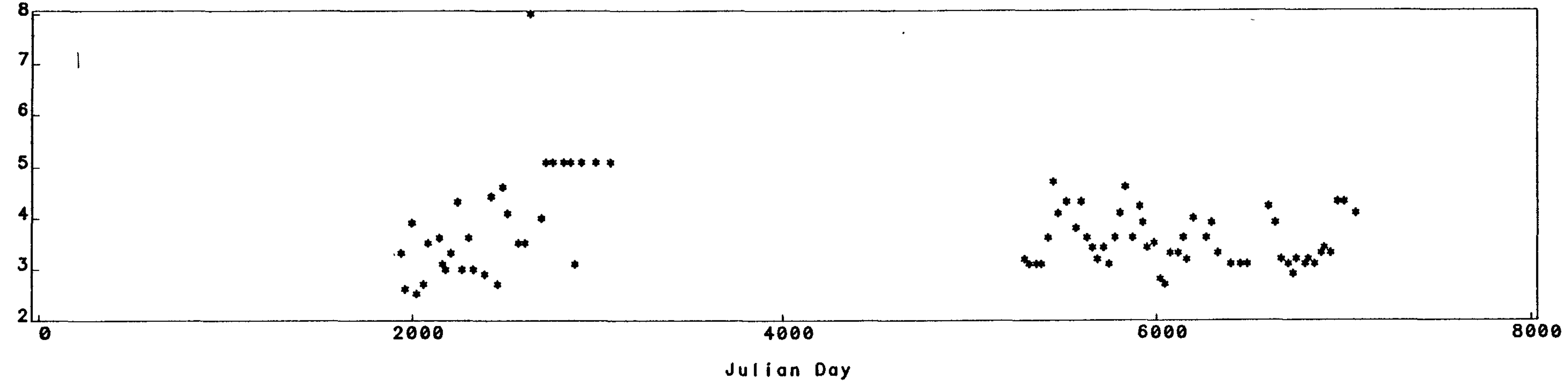
River no 8 SO4-MTB



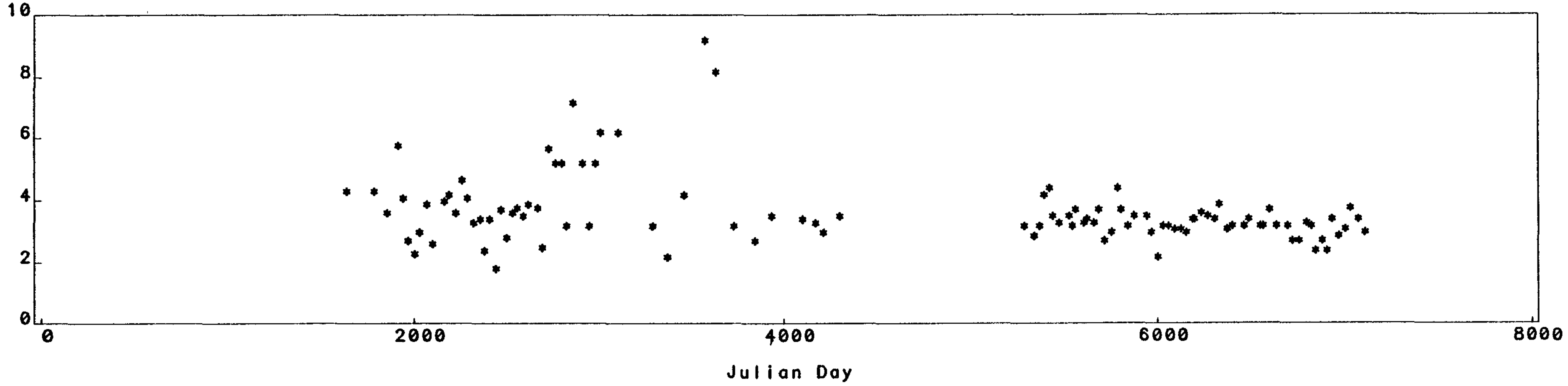
River no 9 SO4-MTB



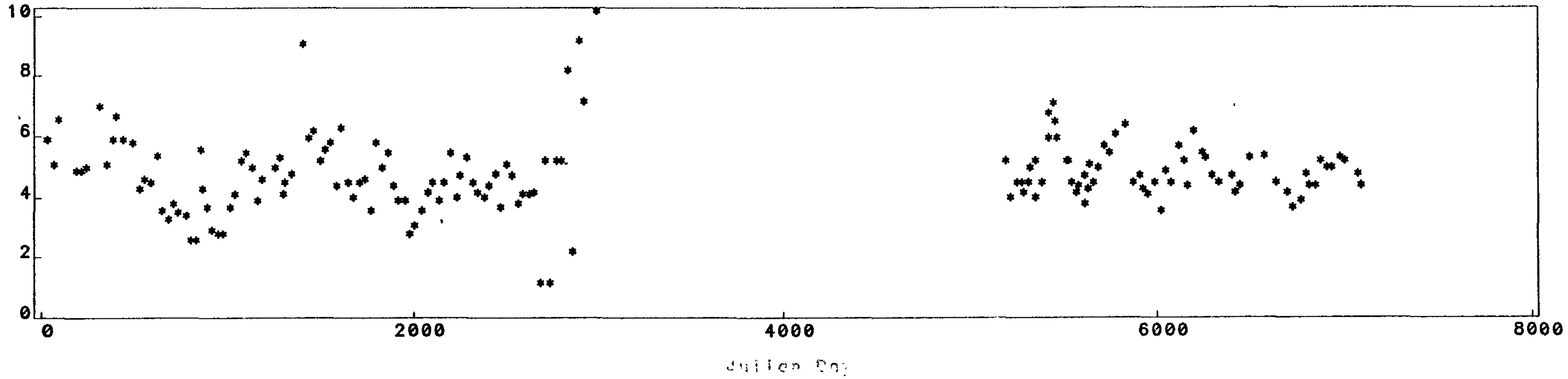
River no 10 SO4-MTB

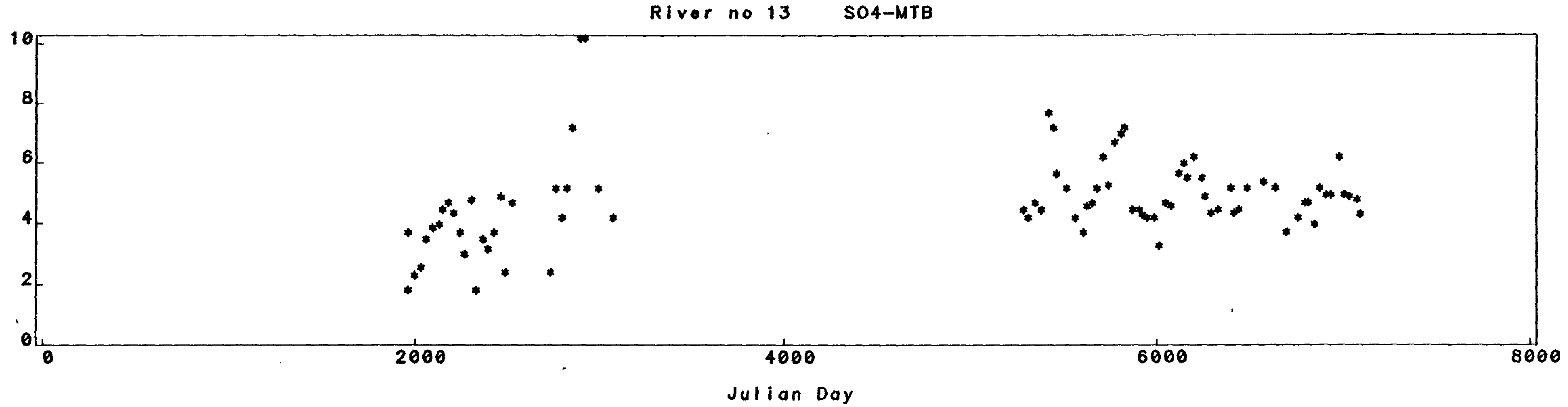


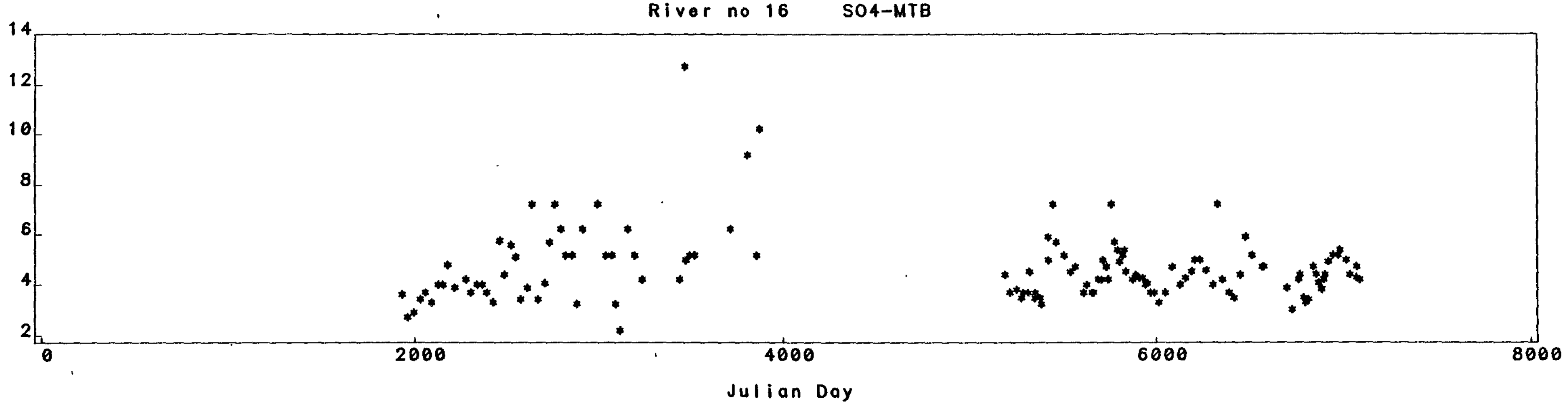
River no 11 SO4-MTB

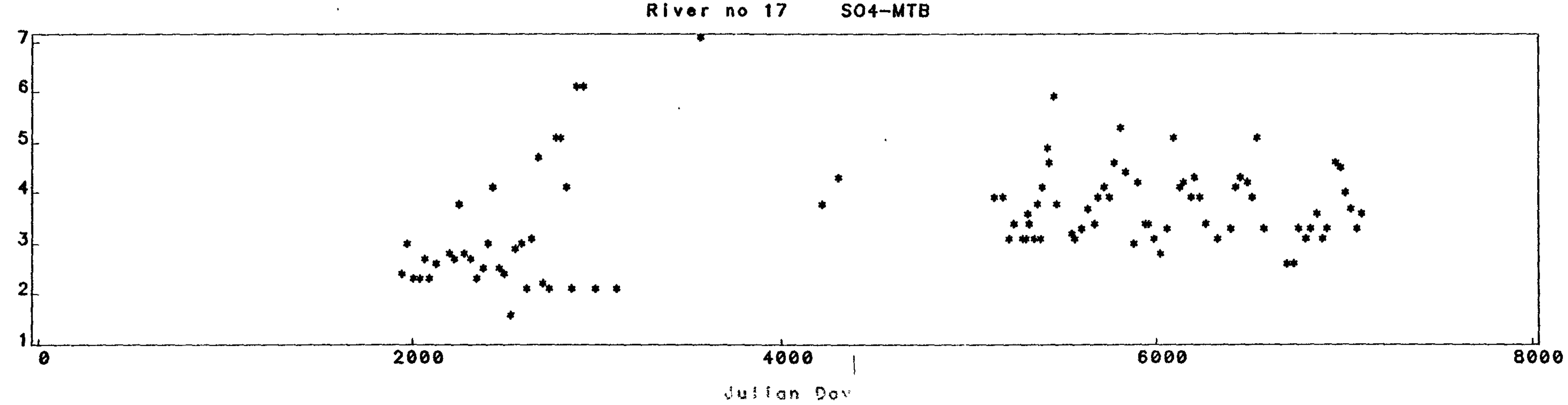


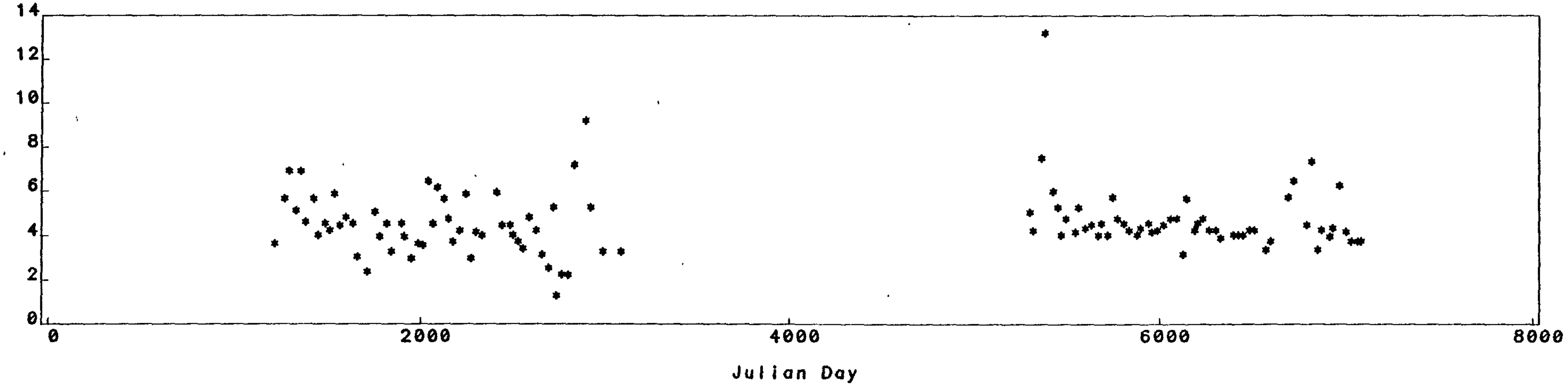
River no 12 SO4-MTB

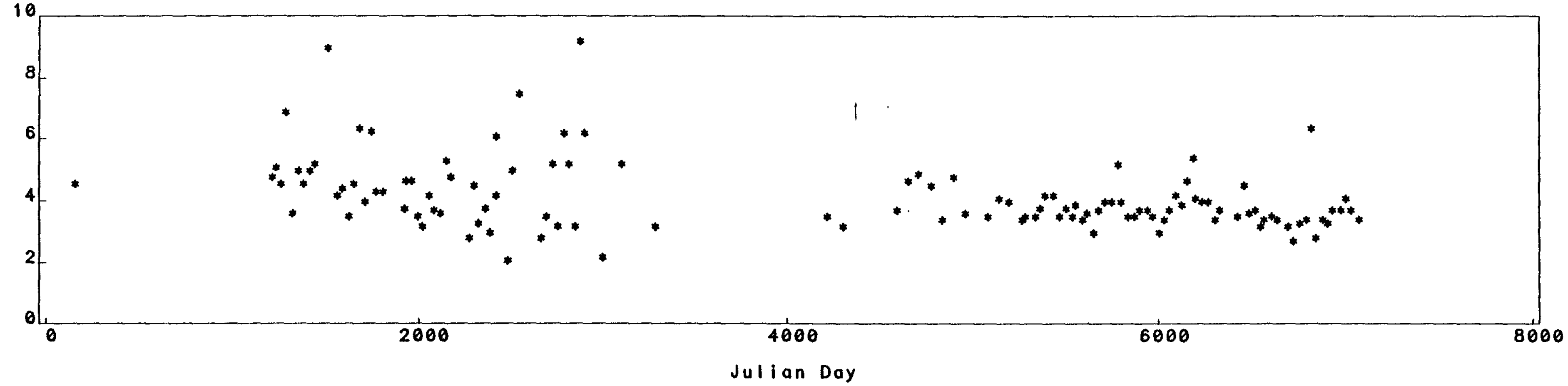


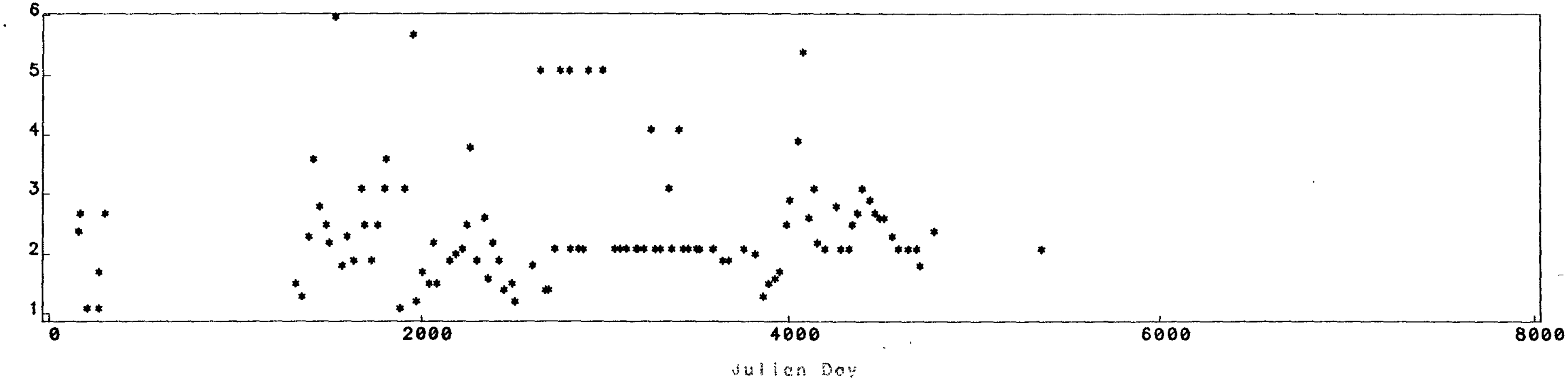

River no 13 SO4-MTB
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

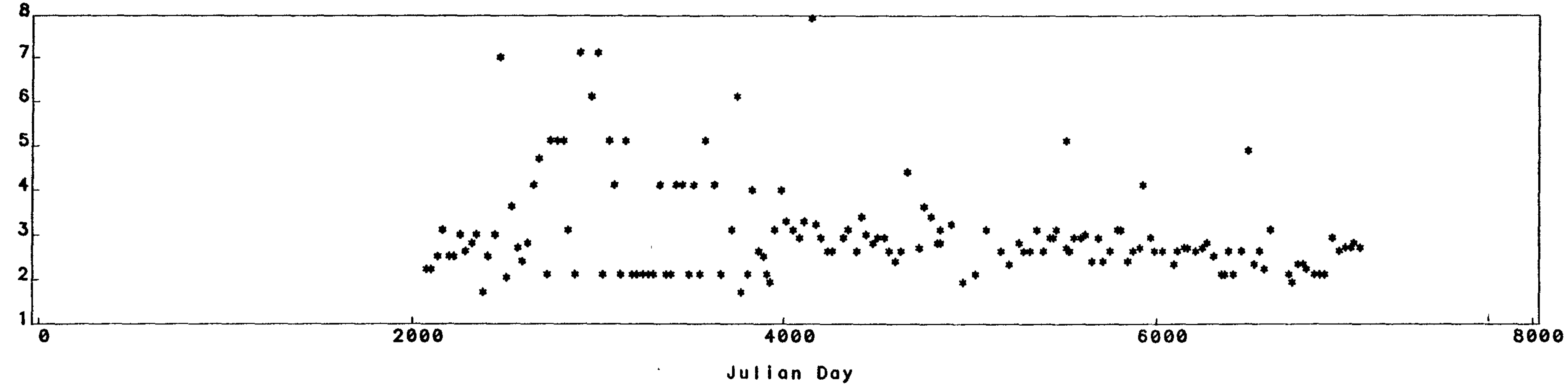

River no 16 SO4-MTB
14
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day

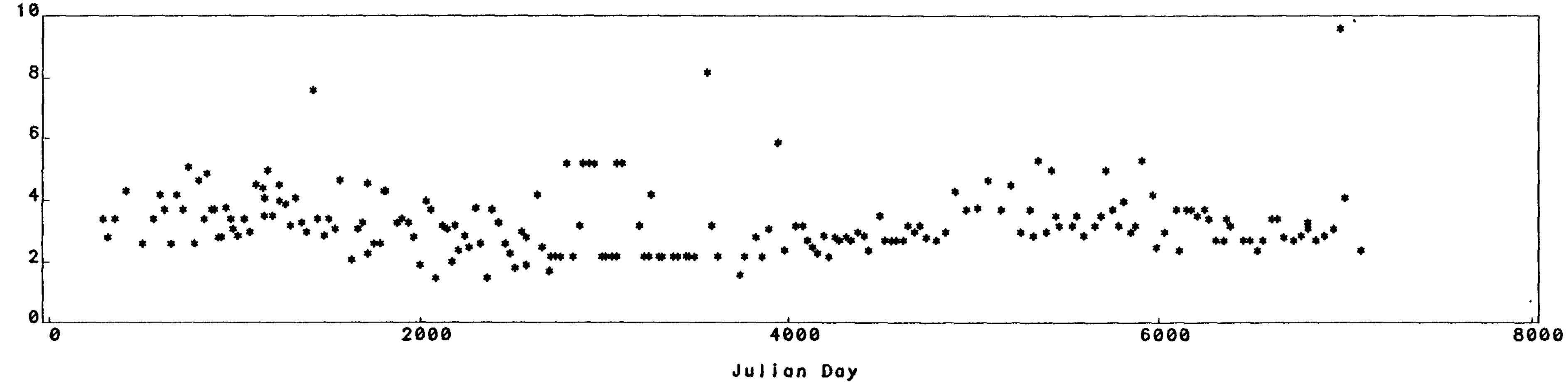

River no 17 SO4-MTB
7
6
5
4
3
2
1
0
2000
4000
6000
8000
Julian Day

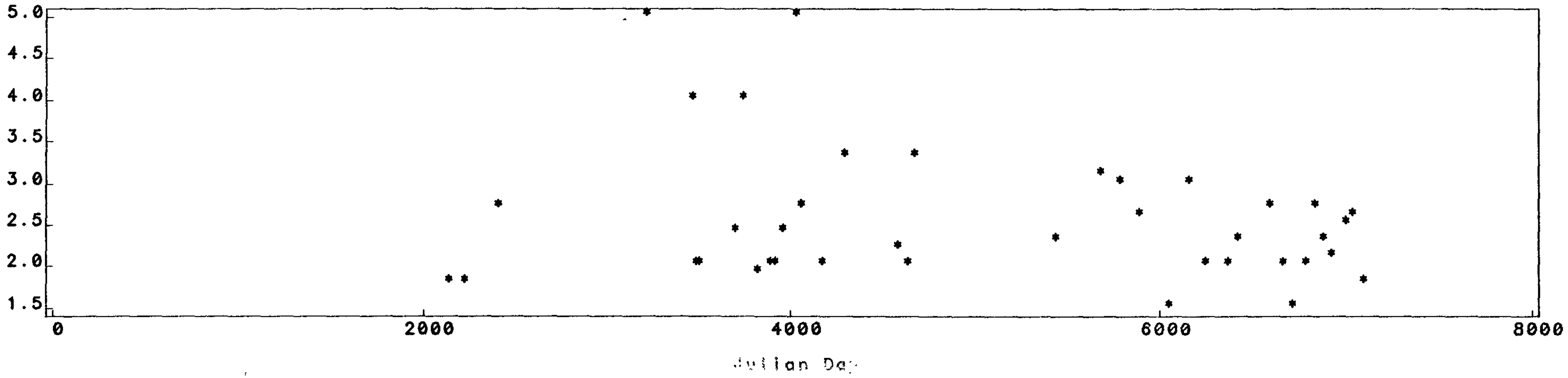

River no 18 SO4-MTB

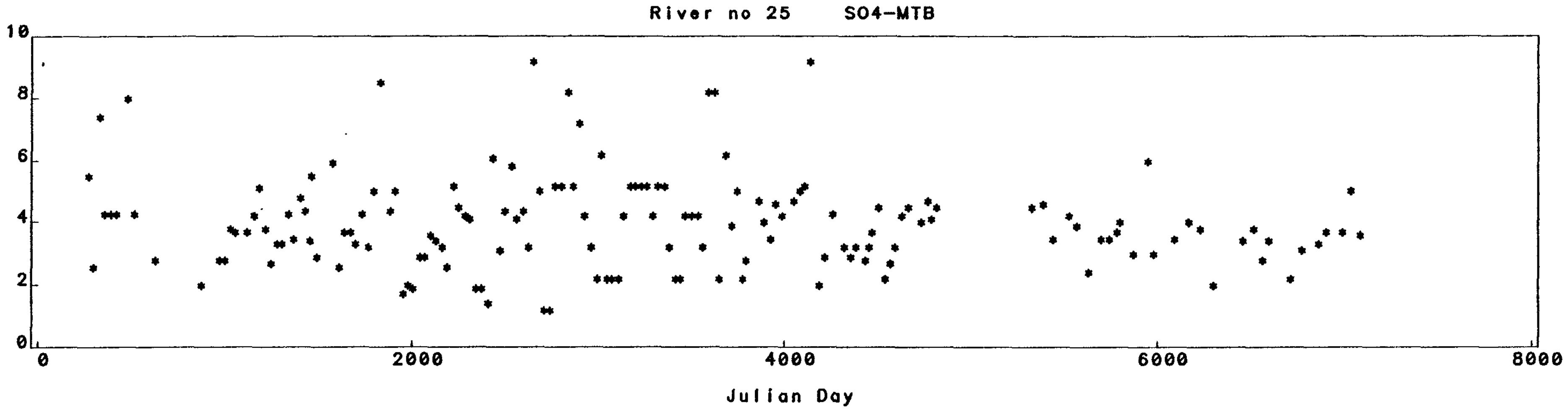

River no 19 SO4-MTB

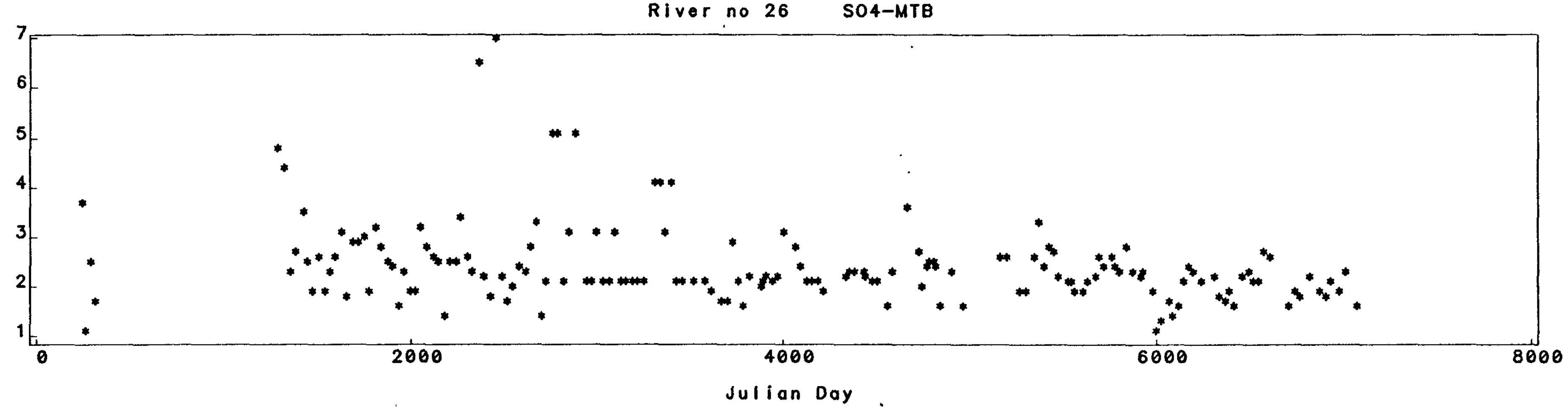

River no 20 SO4-MTB

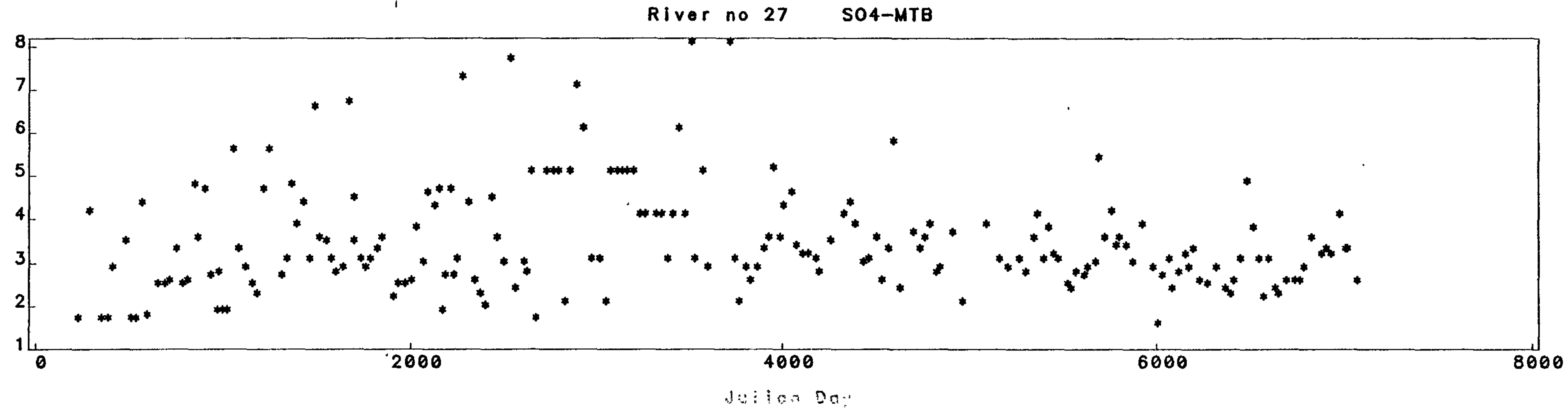

River no 21 SO4-MTB

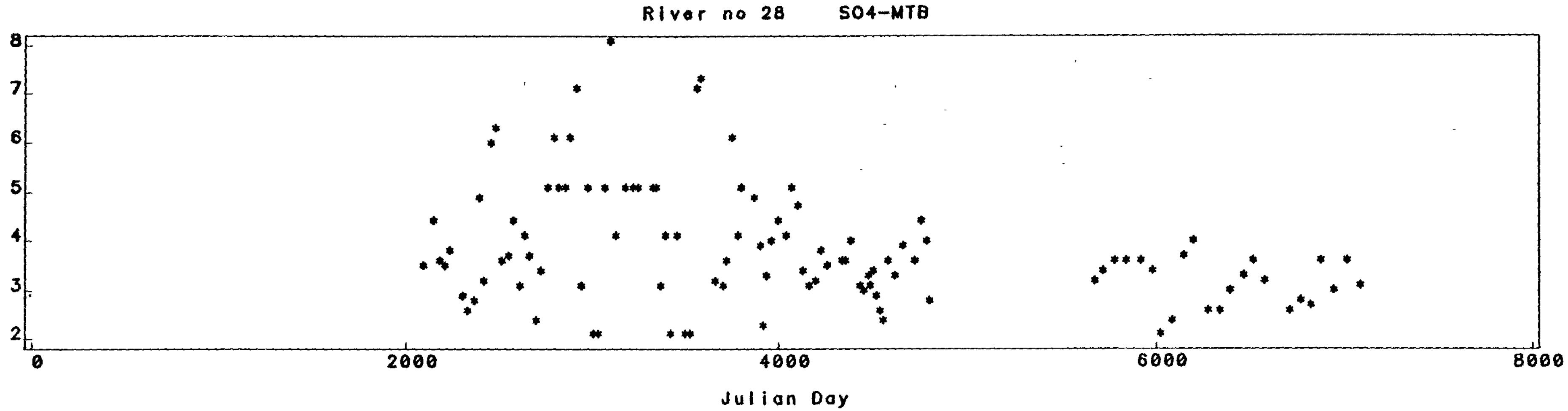

River no 22 SO4-MTB


River no 23 SO4-MTB


River no 25 SO4-MTB
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

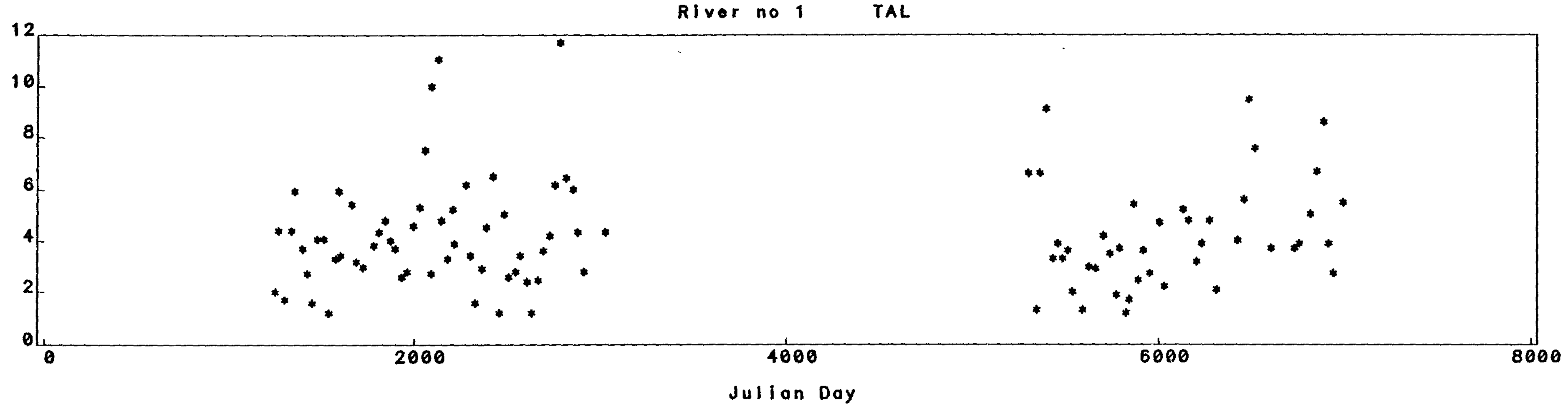

River no 26 SO4-MTB
7
6
5
4
3
2
1
0
2000
4000
6000
8000
Julian Day

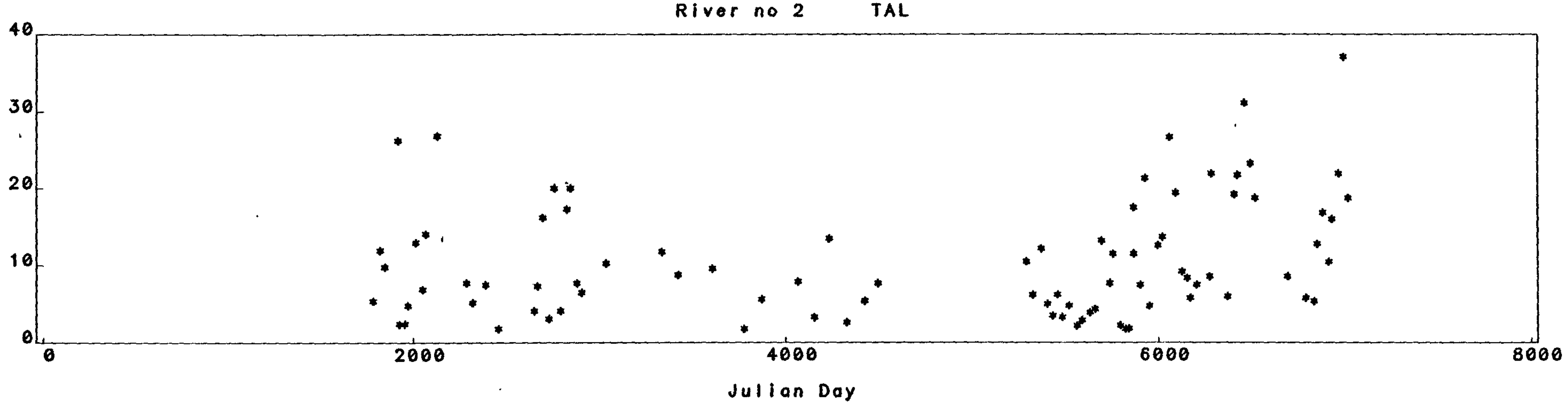

River no 27 SO4-MTB
8
7
6
5
4
3
2
1
0
2000
4000
6000
8000
Julian Day

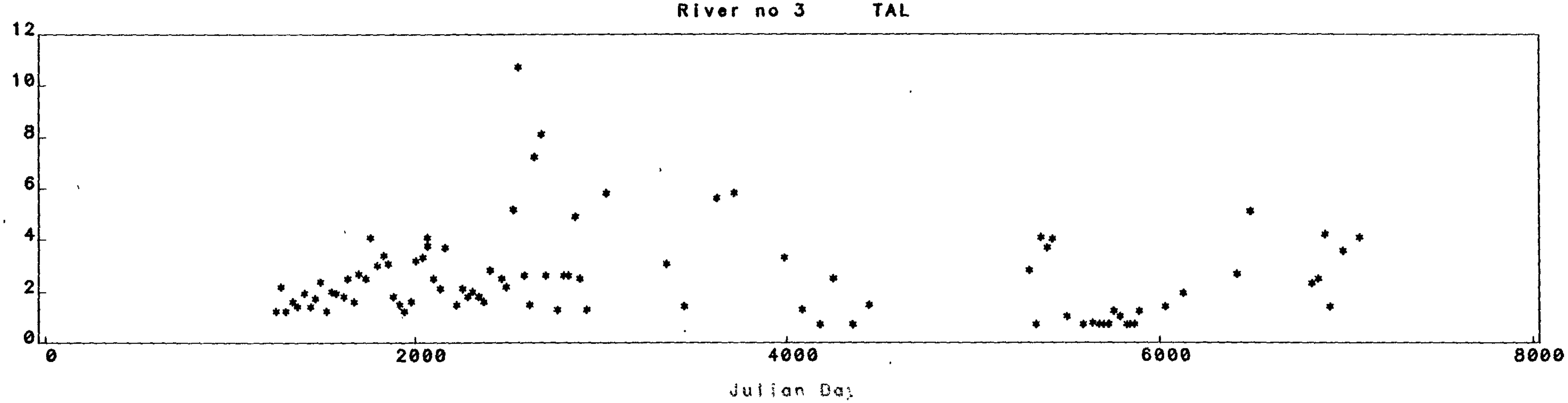


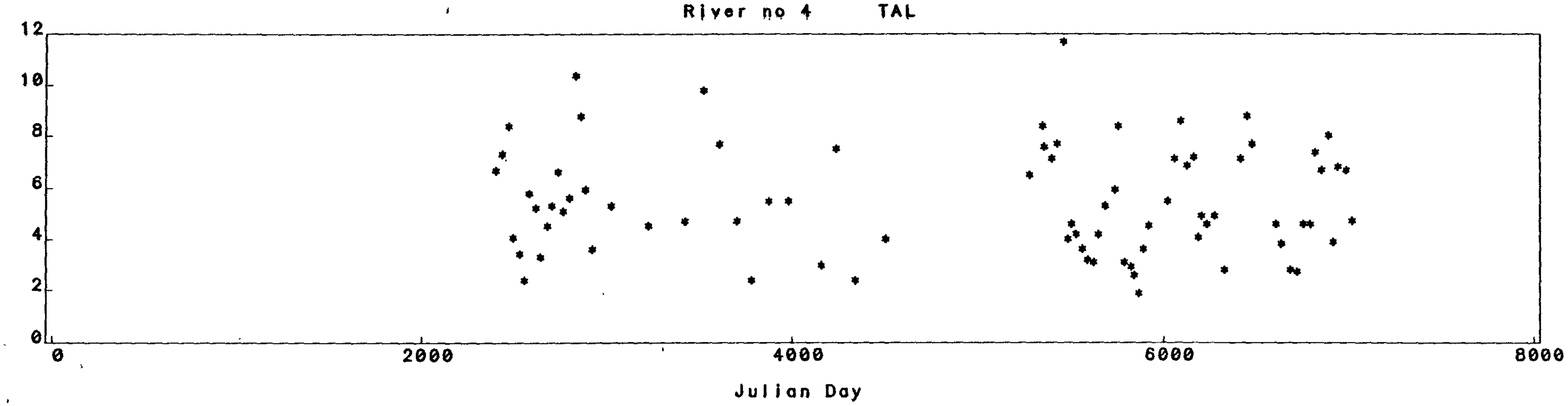
River no 28   SO4-MTB

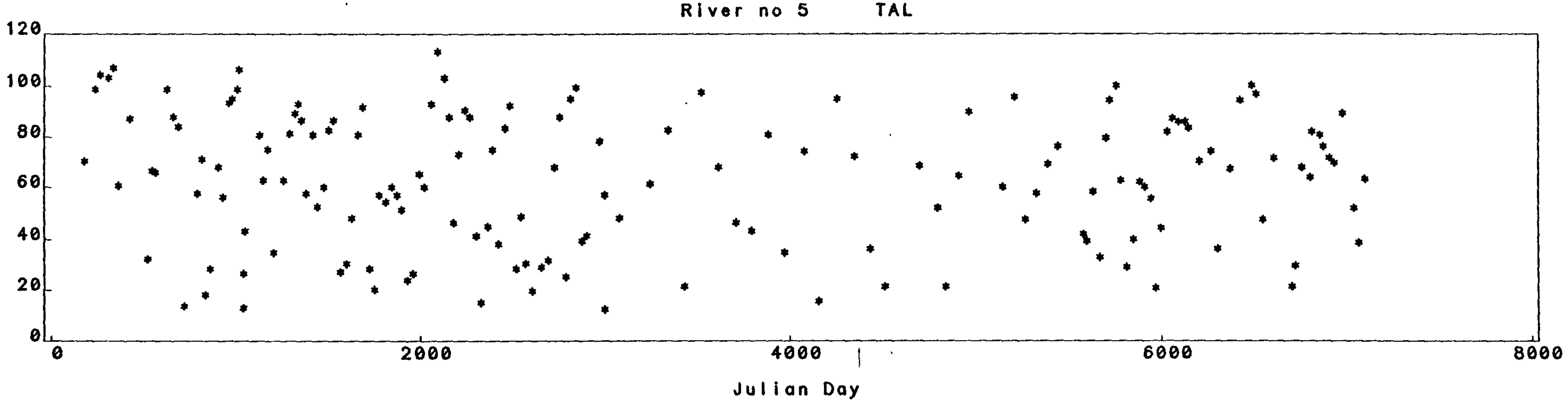
Figure 7. Scatter plots of total alkalinity for the study rivers.

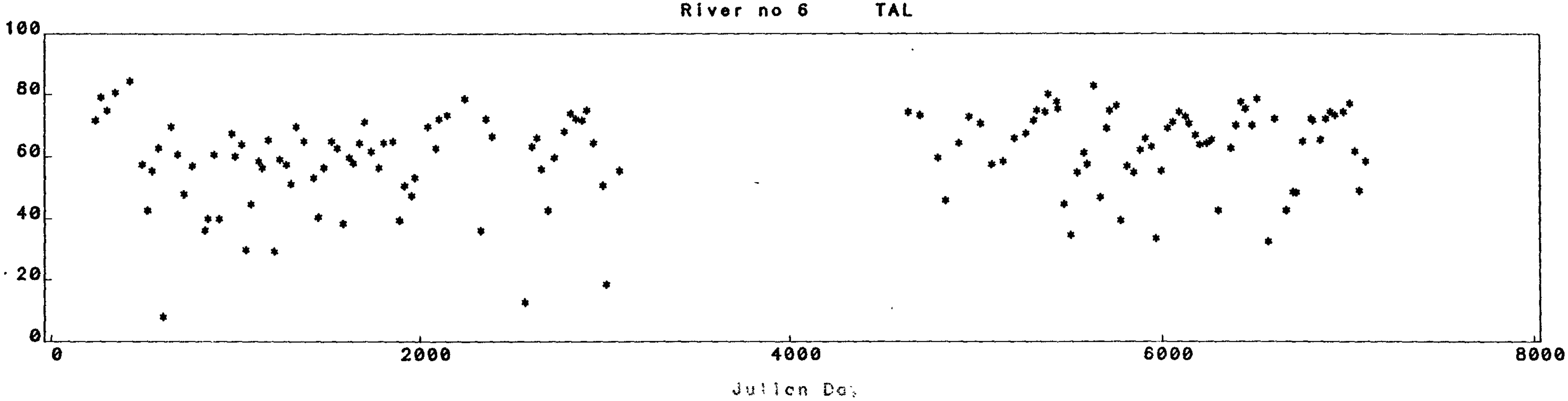

River no 1 TAL
12
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

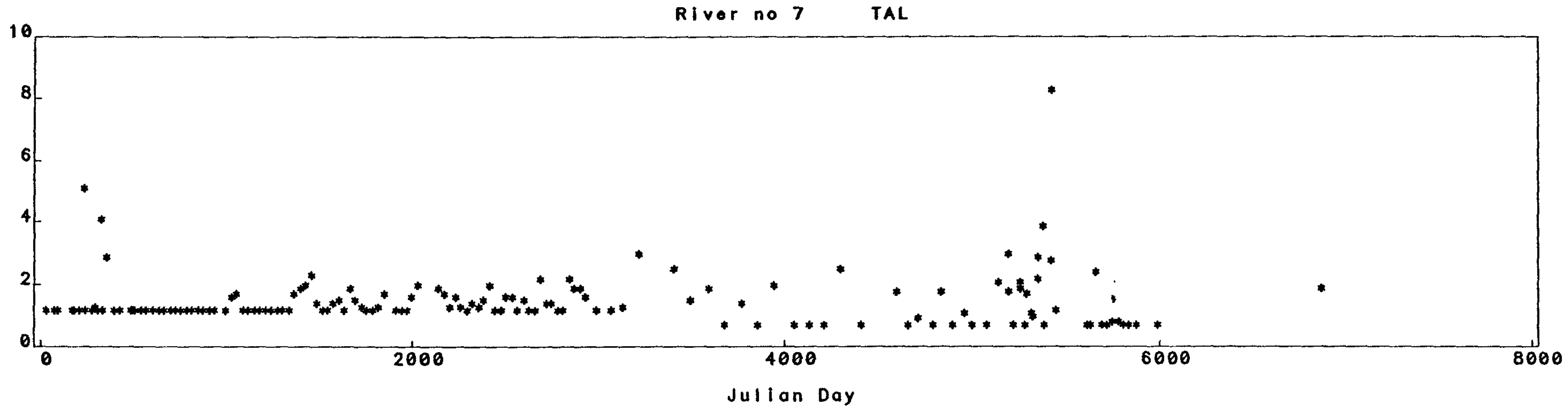

River no 2 TAL
40
30
20
10
0
0
2000
4000
6000
8000
Julian Day

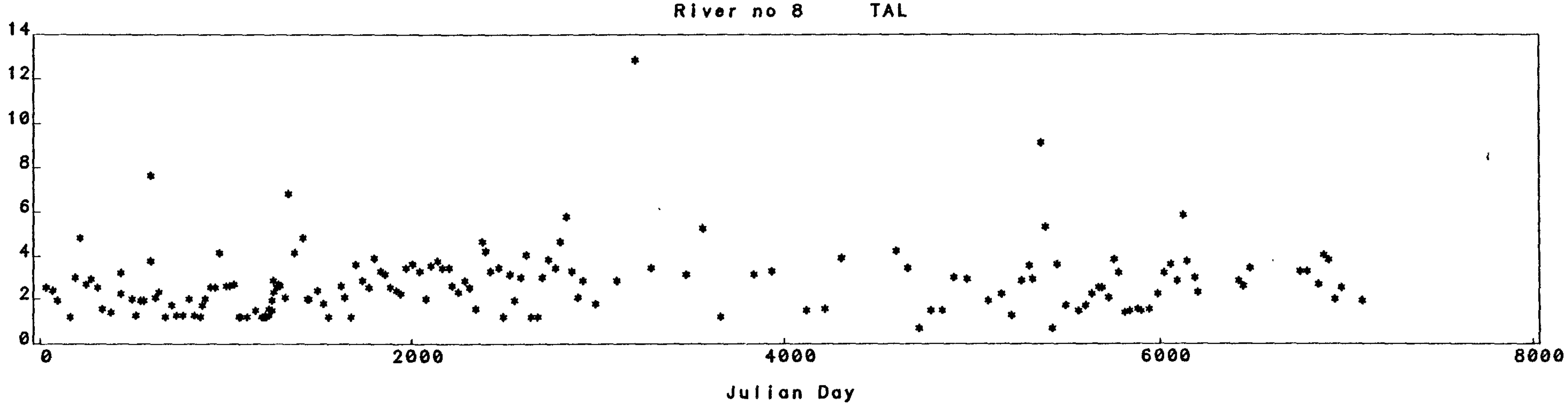

River no 3 TAL
12
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

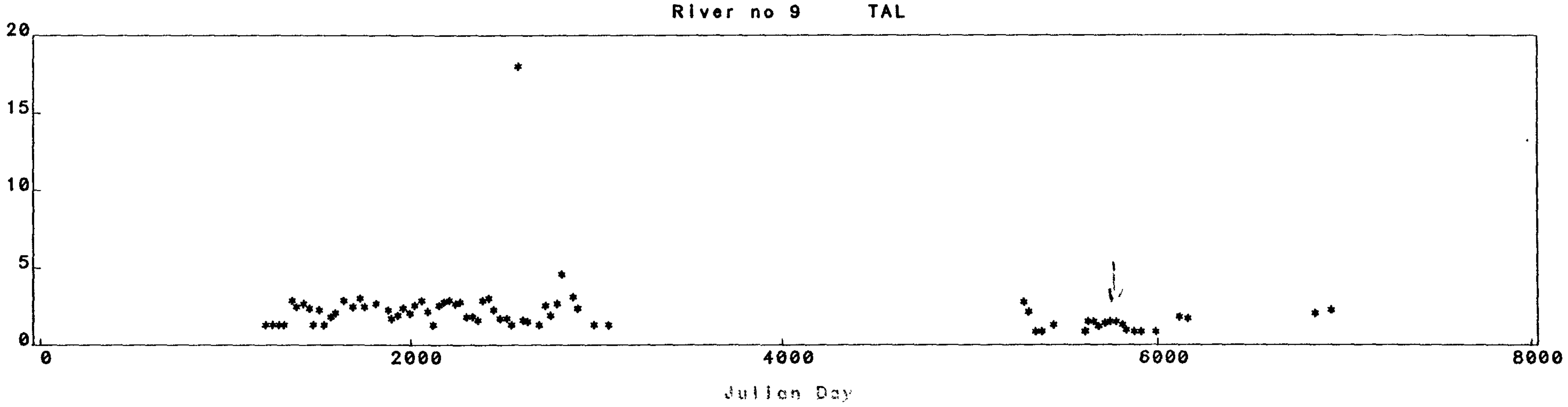

River no 4 TAL
12
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

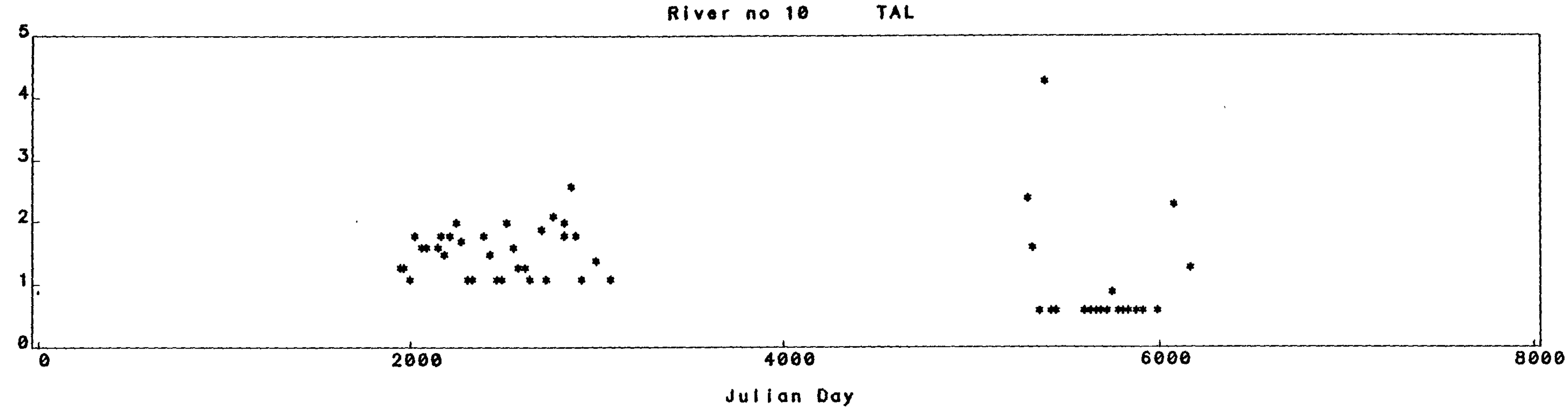

River no 5 TAL
120
100
80
60
40
20
0
0
2000
4000
6000
8000
Julian Day

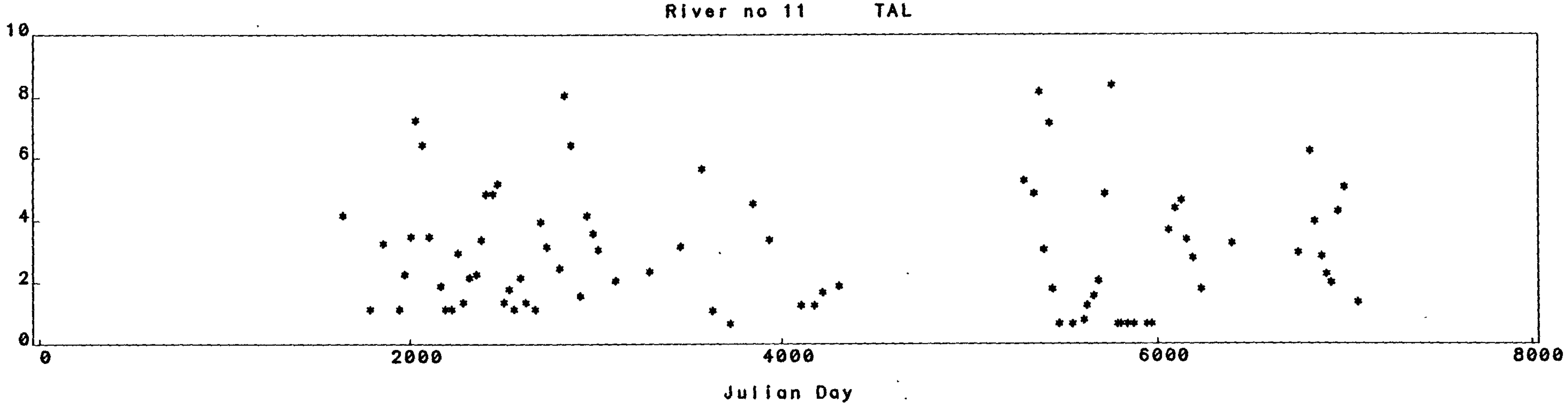

River no 6 TAL
100
80
60
40
20
0
0
2000
4000
6000
8000
Julian Day

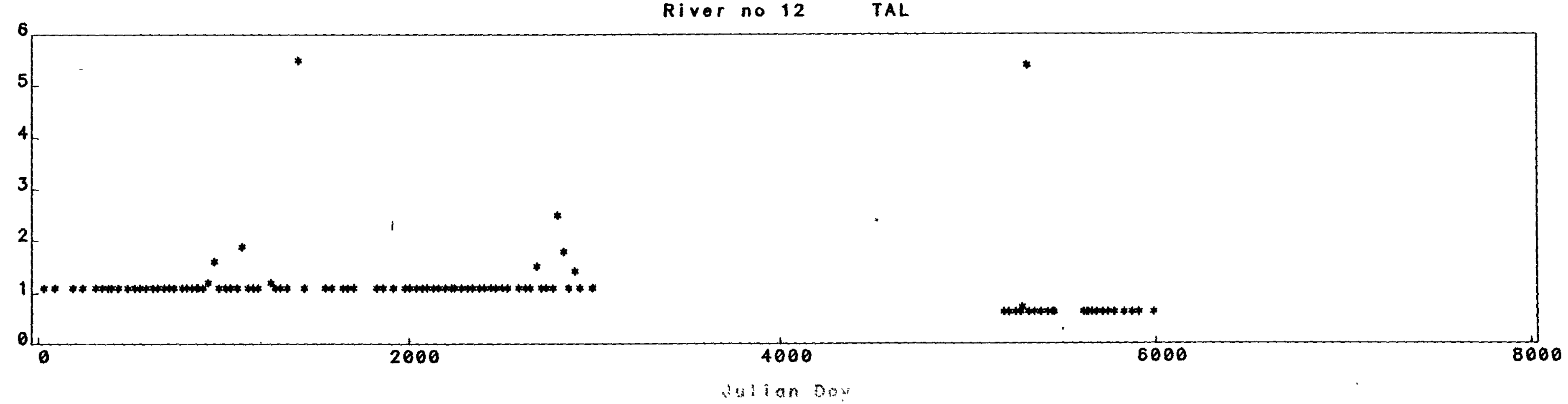

River no 7 TAL
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

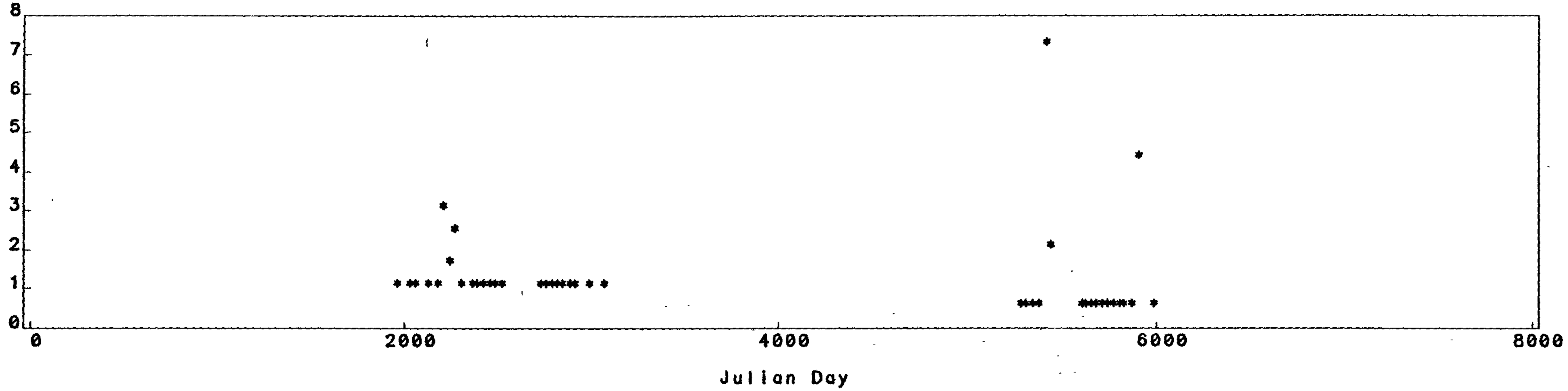

River no 8 TAL
14
12
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day


River no 9 TAL
20
15
10
5
0
0
2000
4000
6000
8000
Julian Day

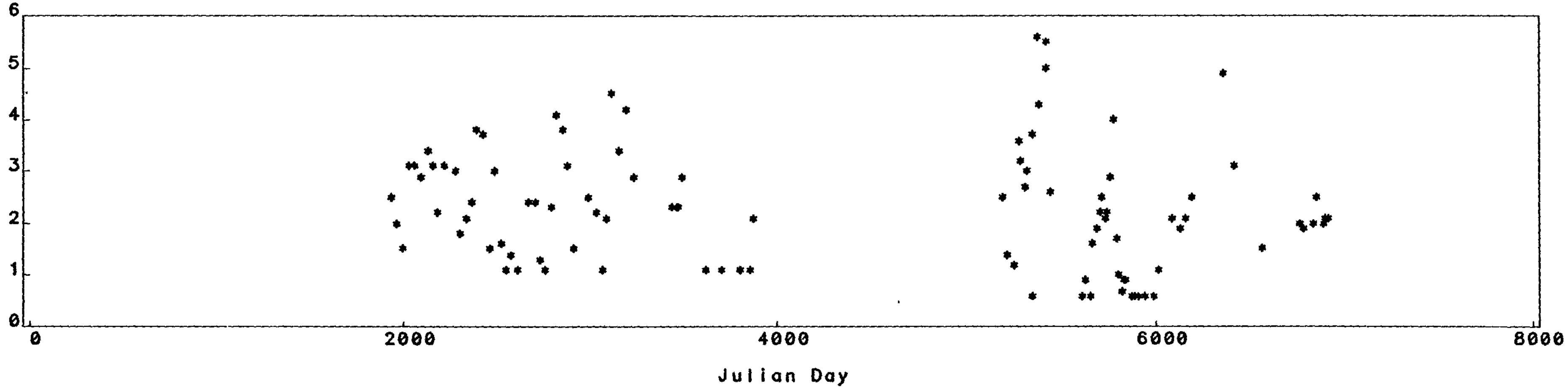

River no 10 TAL
5
4
3
2
1
0
0
2000
4000
6000
8000
Julian Day


River no 11 TAL
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

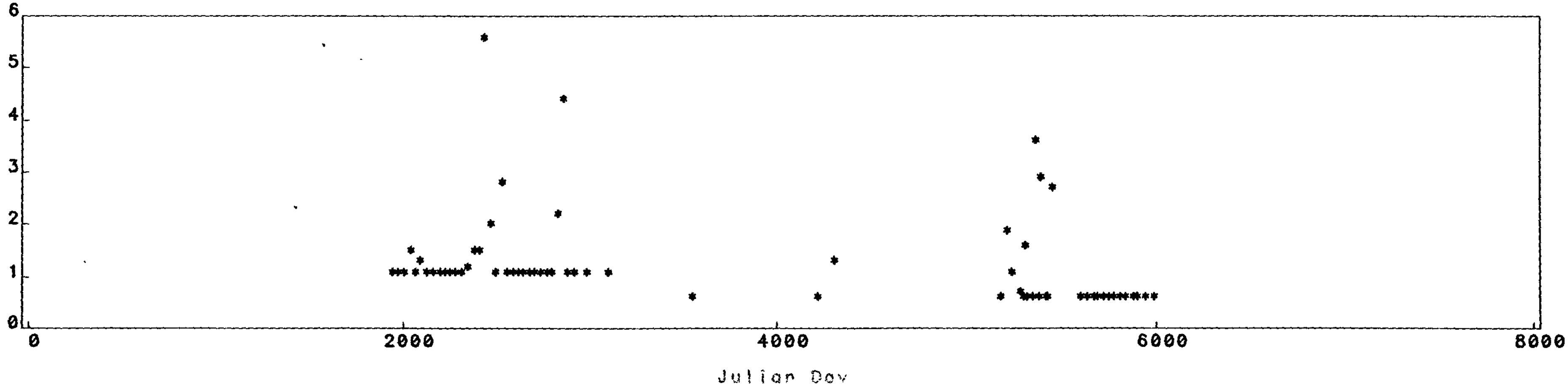

River no 12 TAL
6
5
4
3
2
1
0
0
2000
4000
6000
8000
Julian Day



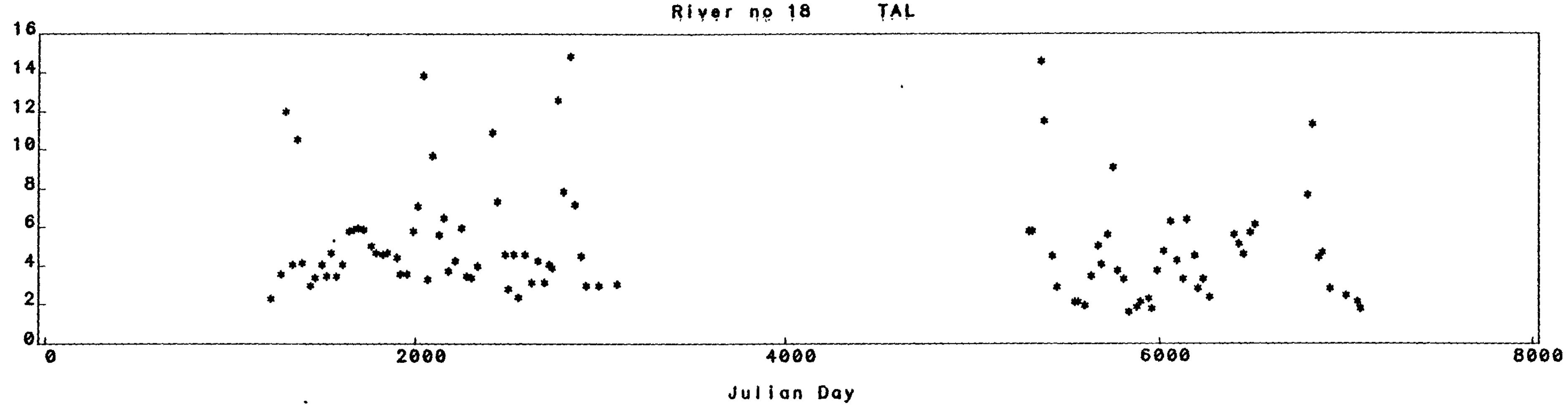
River no 13 TAL

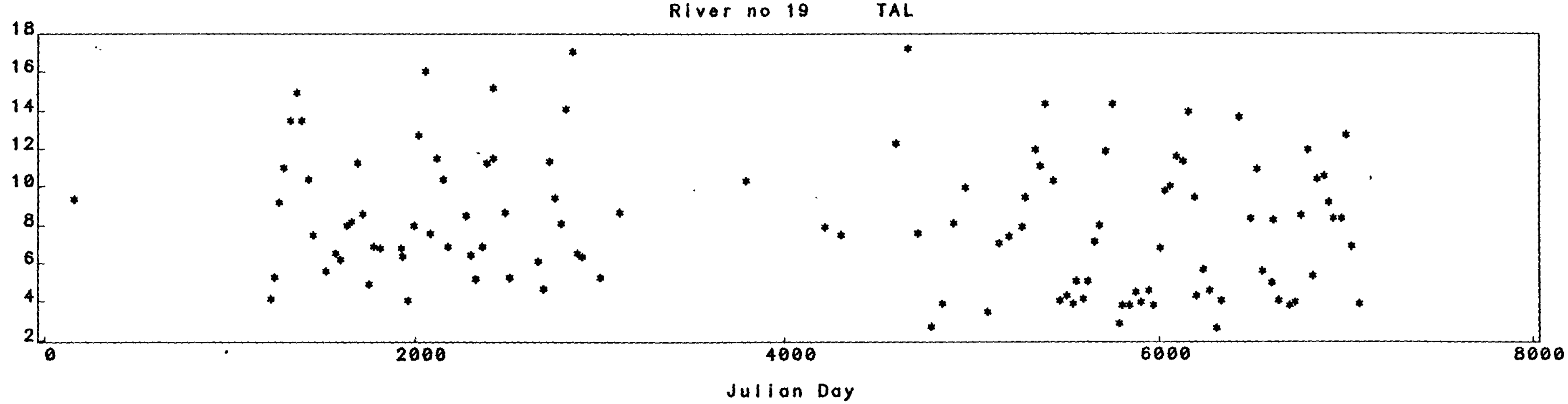


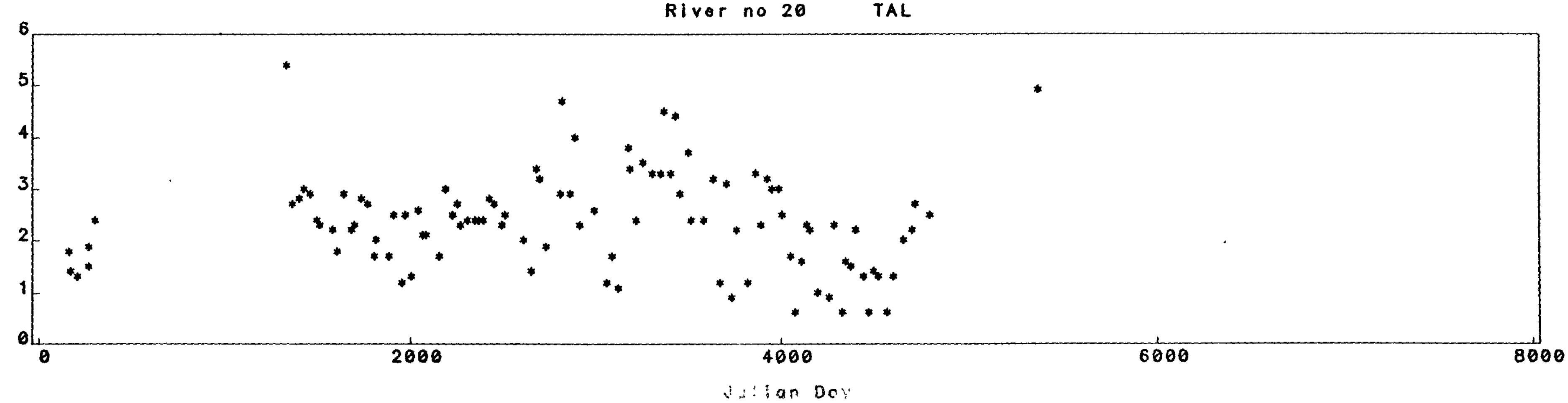
River no 16 TAL



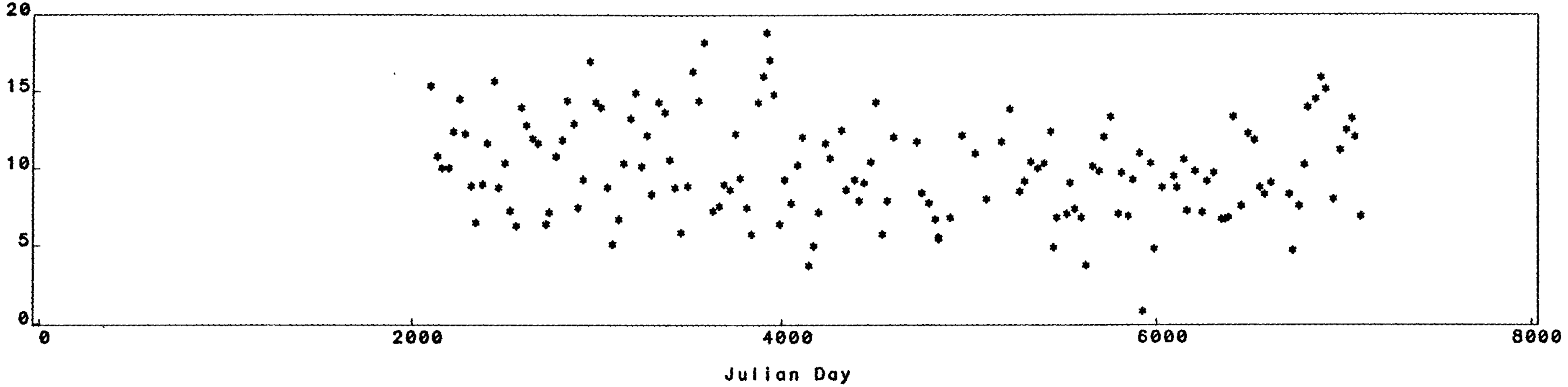
River no 17 TAL


River no 18 TAL
16
14
12
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

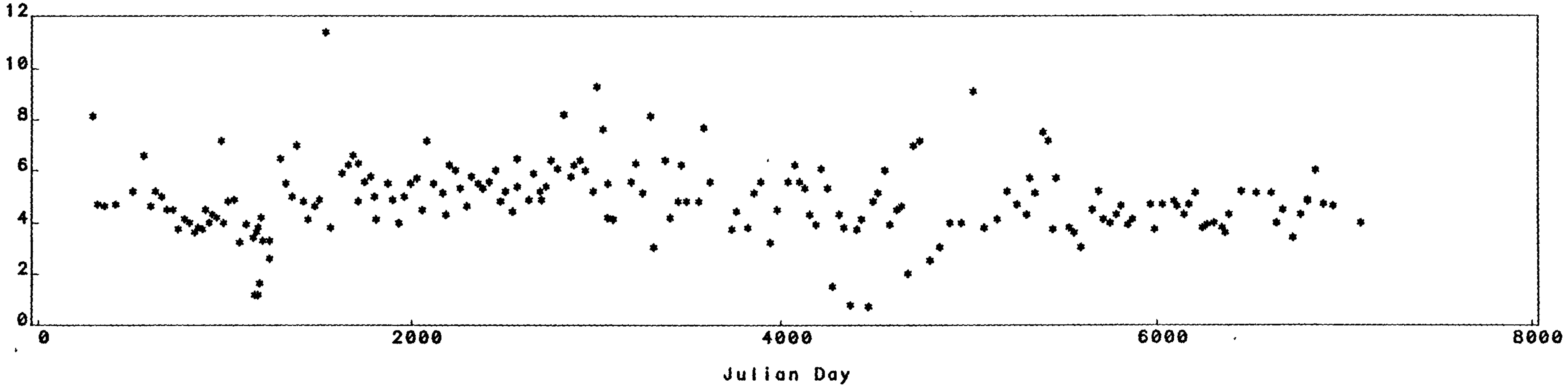

River no 19 TAL
18
16
14
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day


River no 20 TAL
6
5
4
3
2
1
0
0
2000
4000
6000
8000
Julian Day

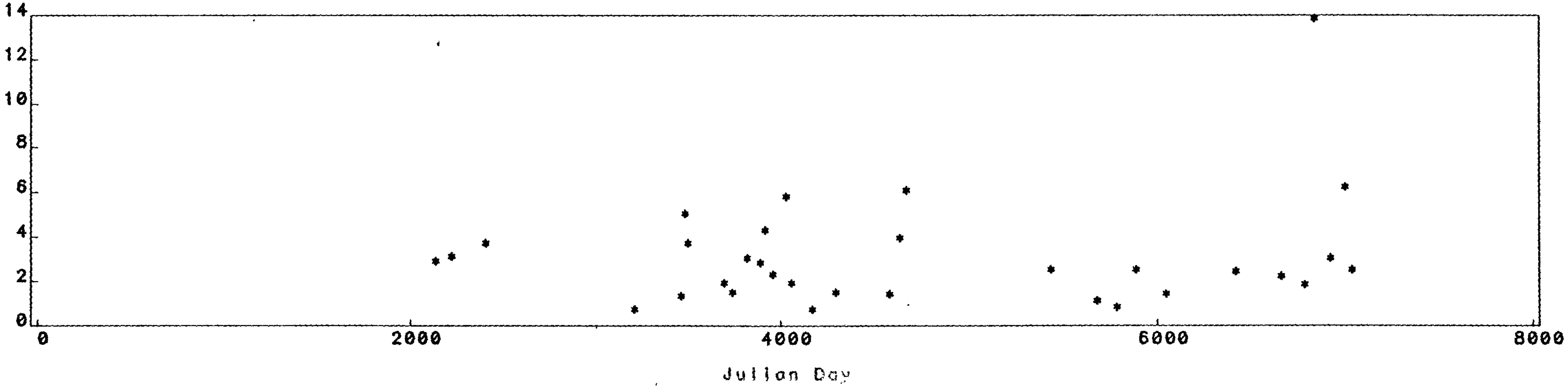
River no 21 TAL



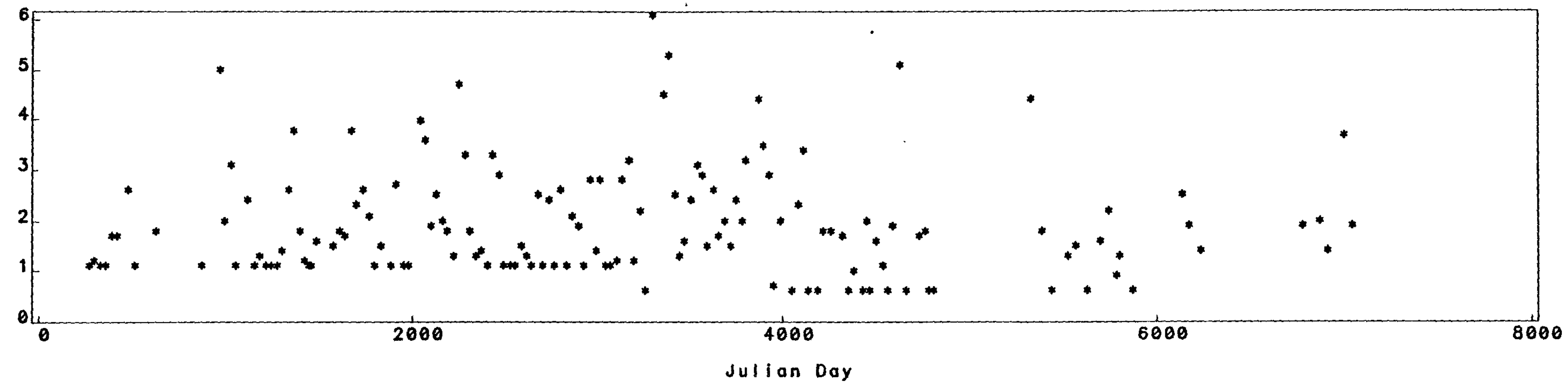
River no 22 TAL



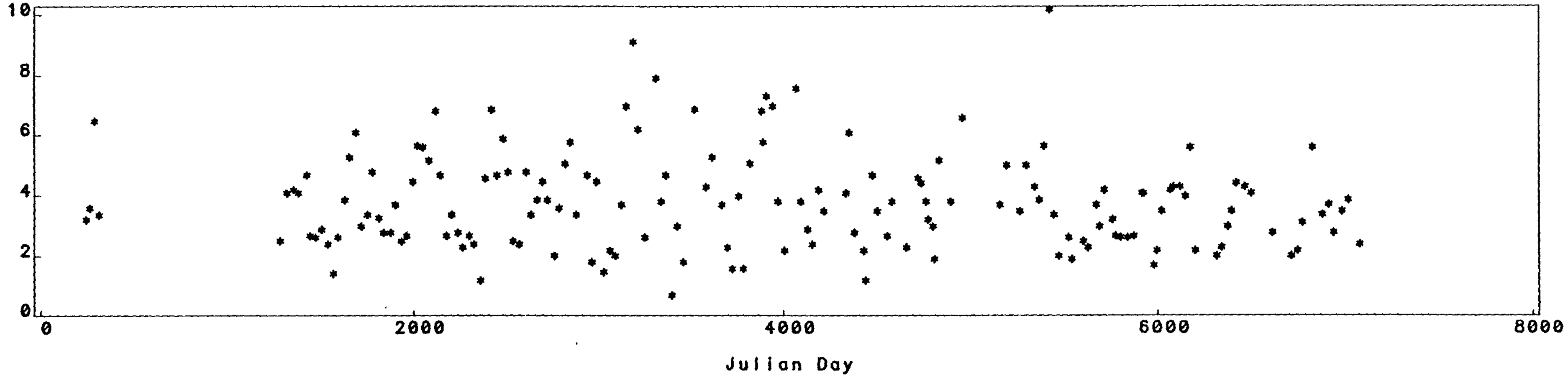
River no 23 TAL



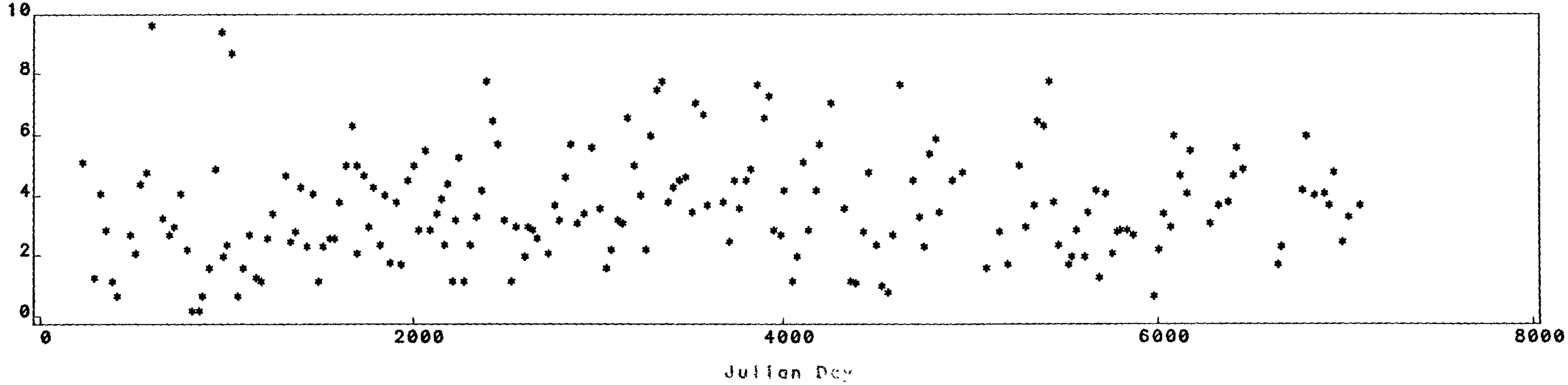
River no 25 TAL



River no 26 TAL



River no 27 TAL



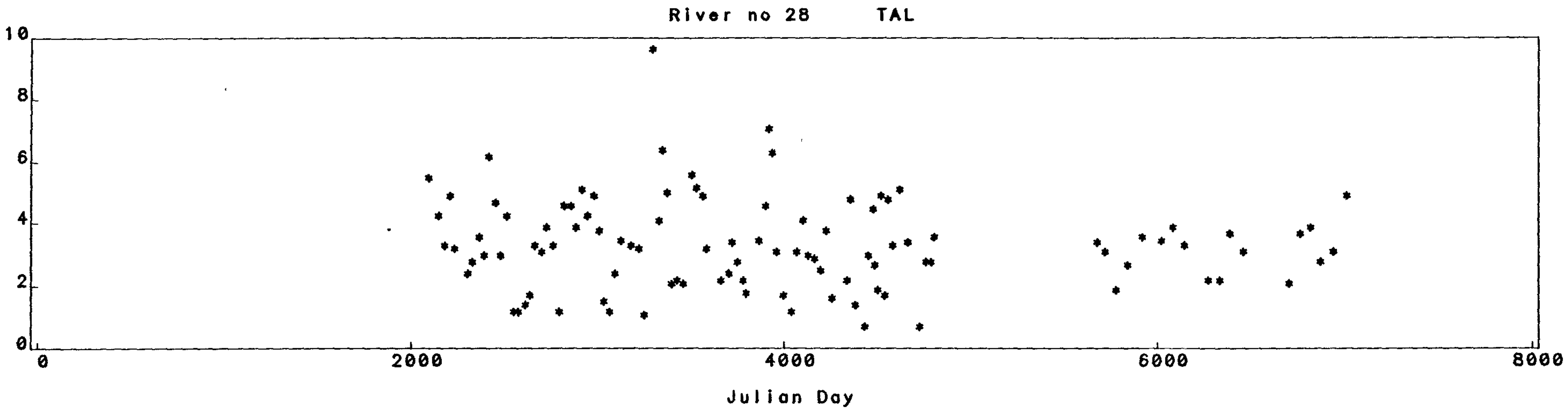
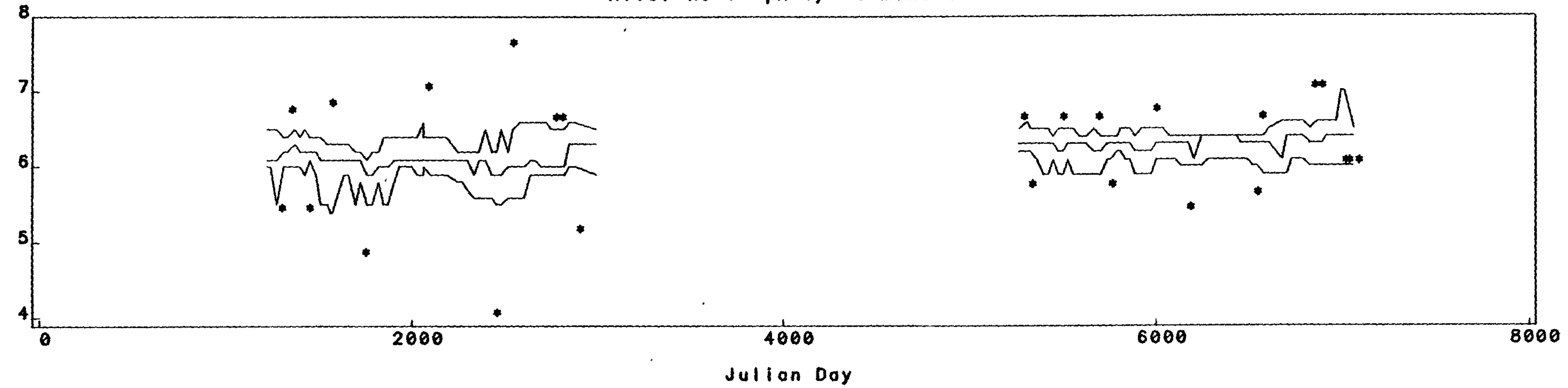
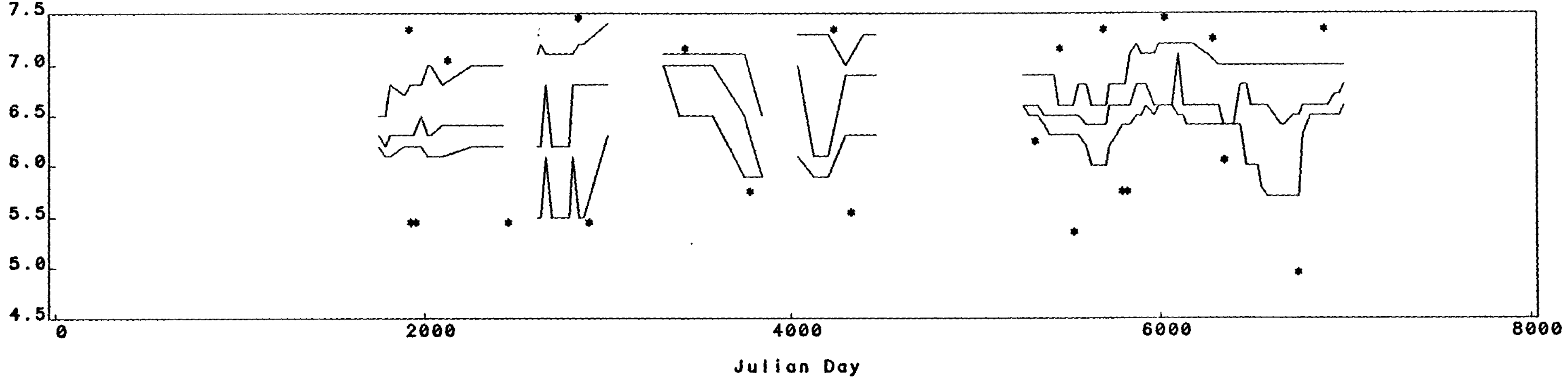

River no 28 TAL
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day

Figure 8. Running boxplots of pH for the study rivers.

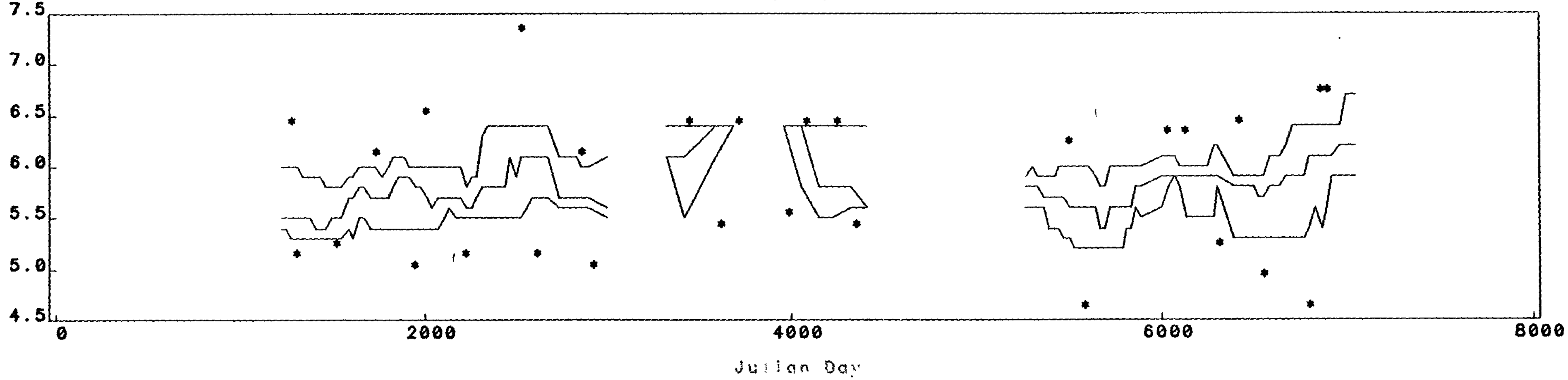
River no 1 pH +/- 6 months

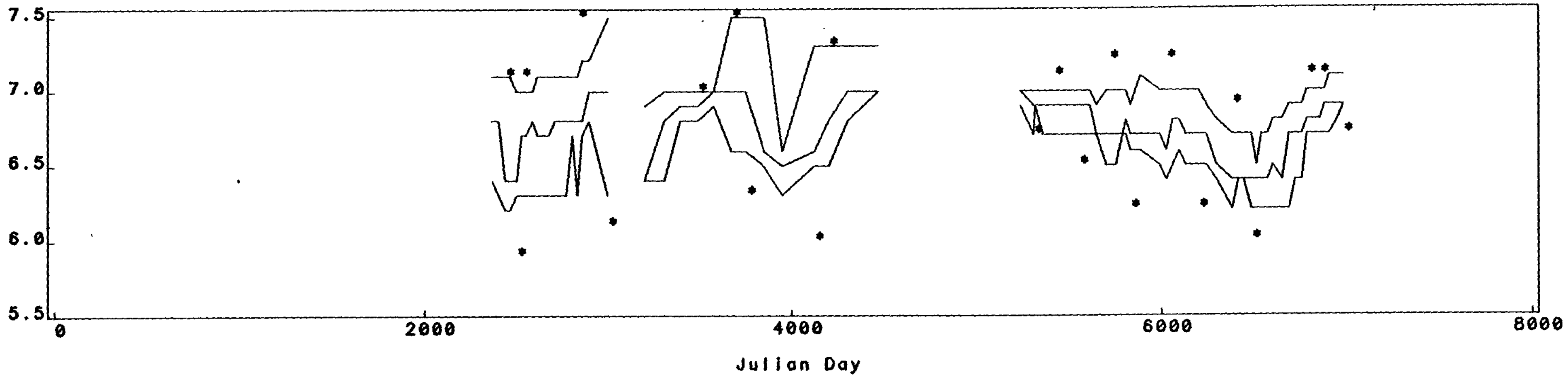


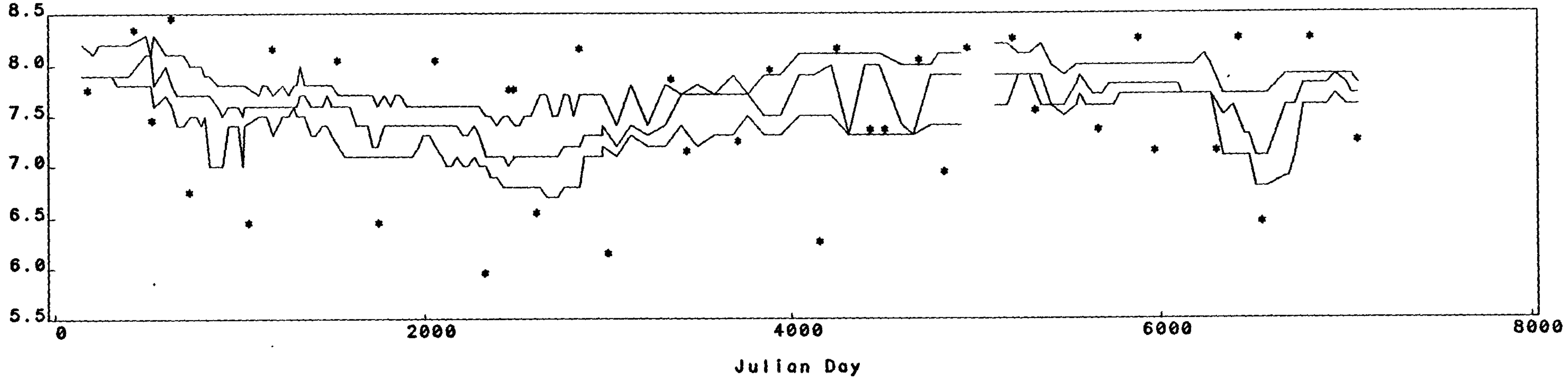
River no 2 pH +/- 6 months

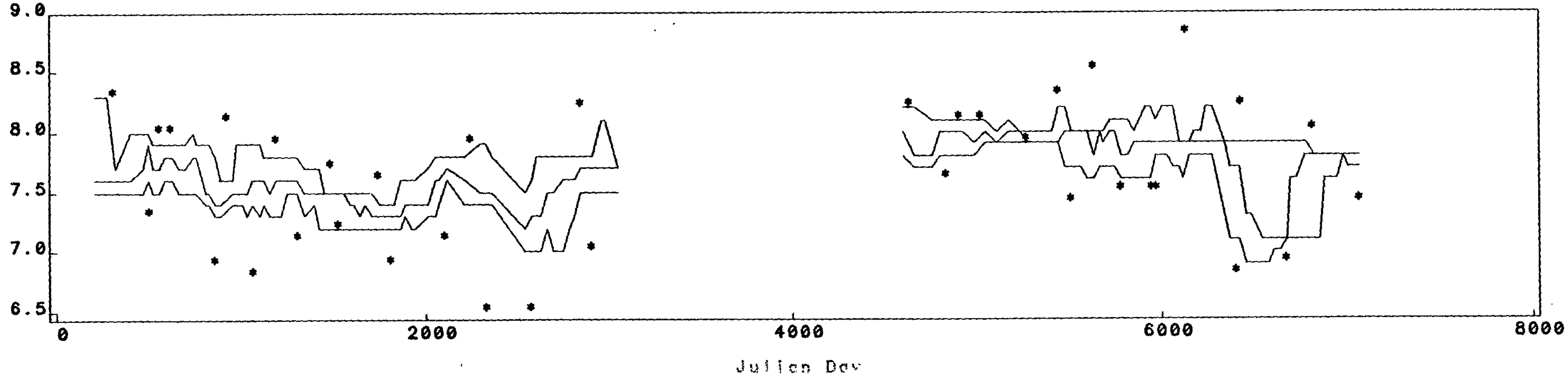


River no 3 pH +/- 6 months

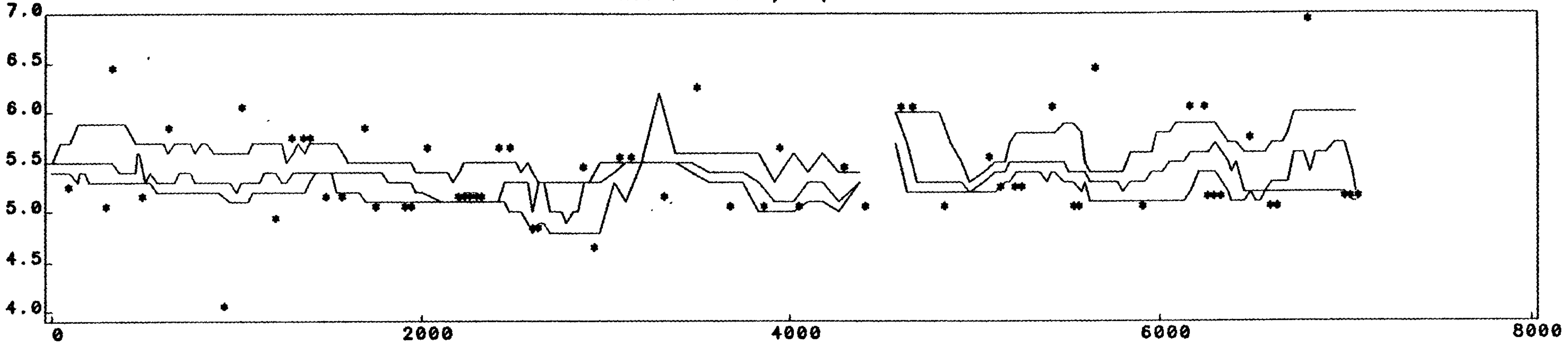



River no 4 pH +/- 6 months

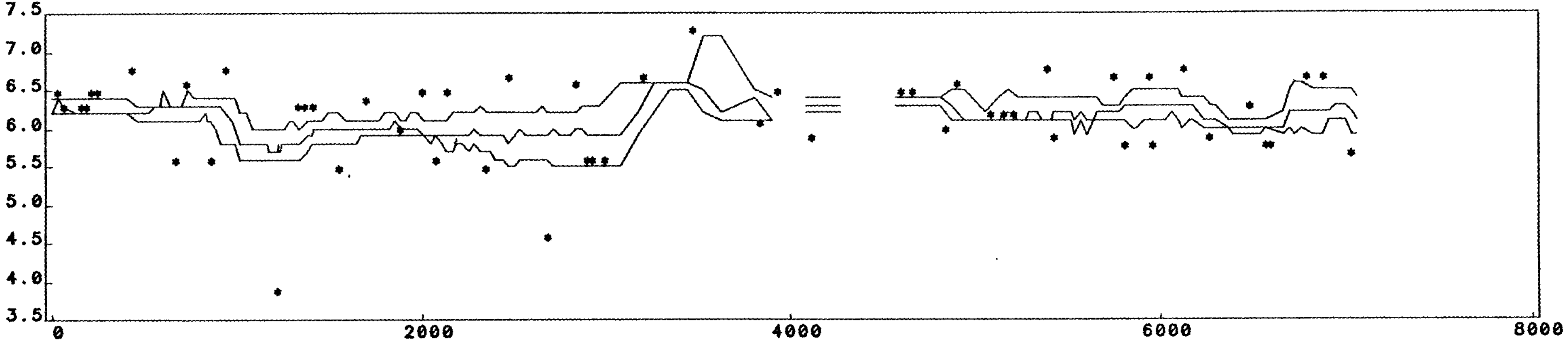

River no 5 pH +/- 6 months


River no 6 pH +/- 6 months

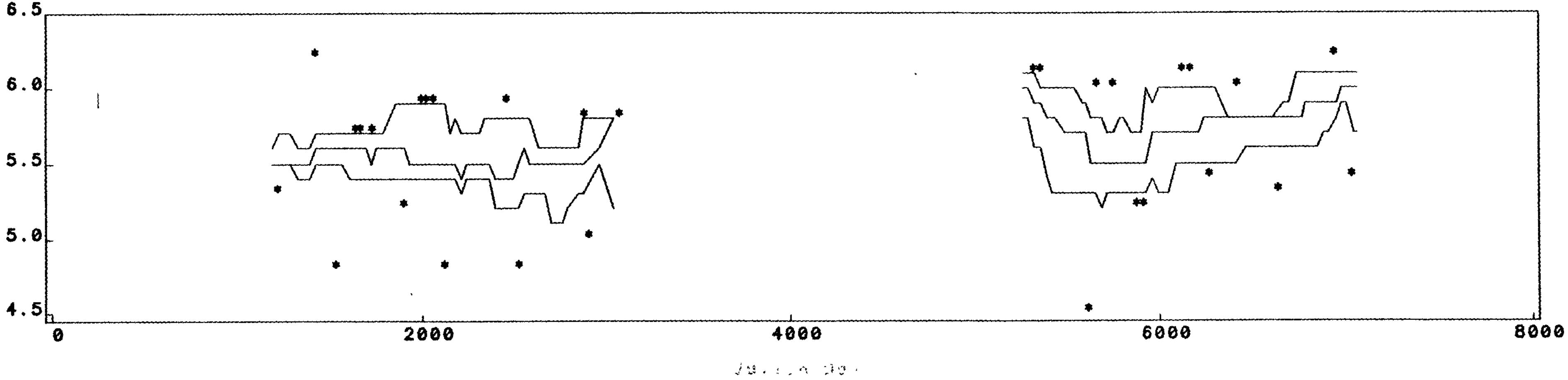
River no 7 pH +/- 6 months



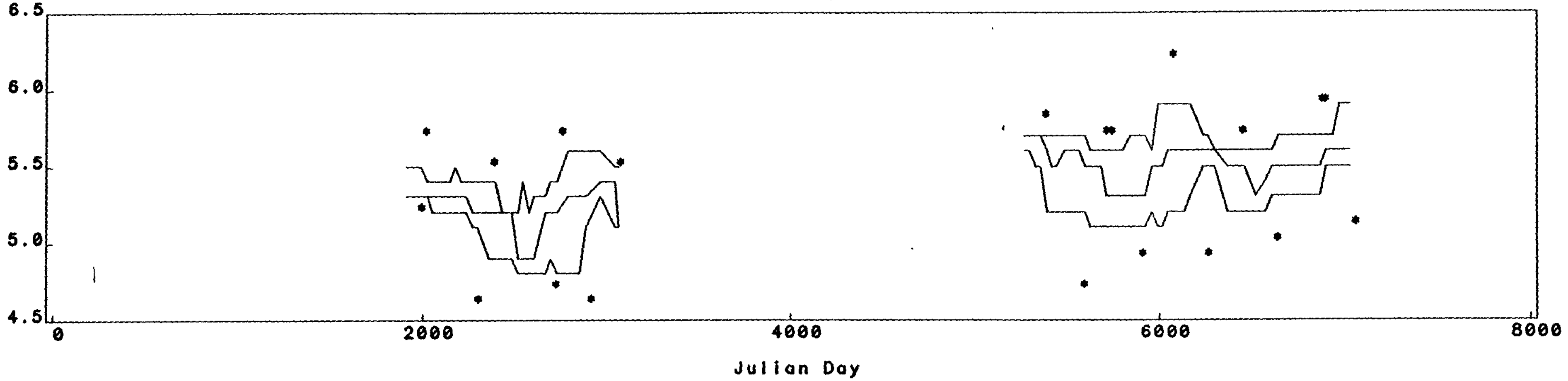
River no 8 pH +/- 6 months



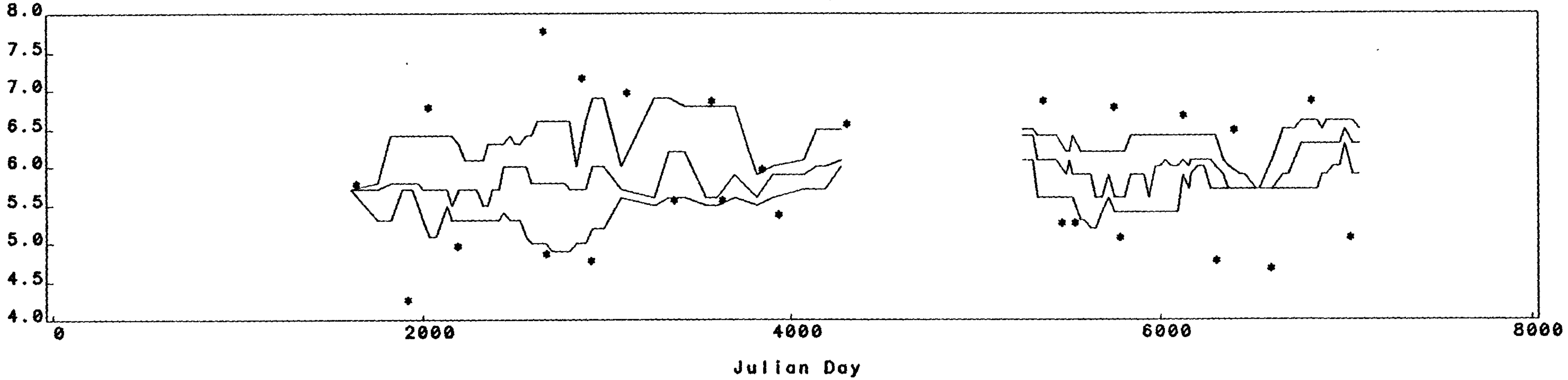
River no 9 pH +/- 6 months



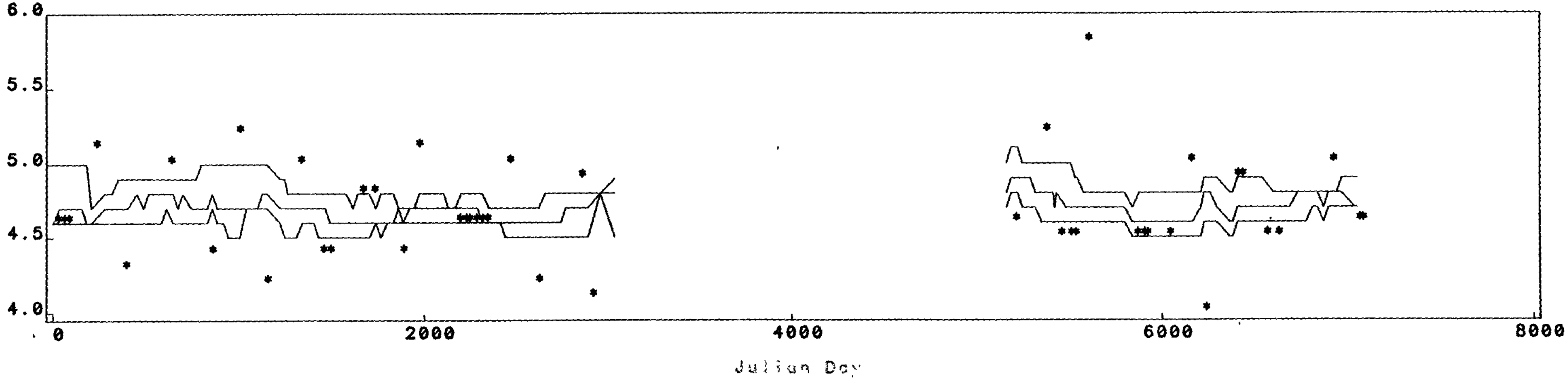
River no 10 pH +/- 6 months

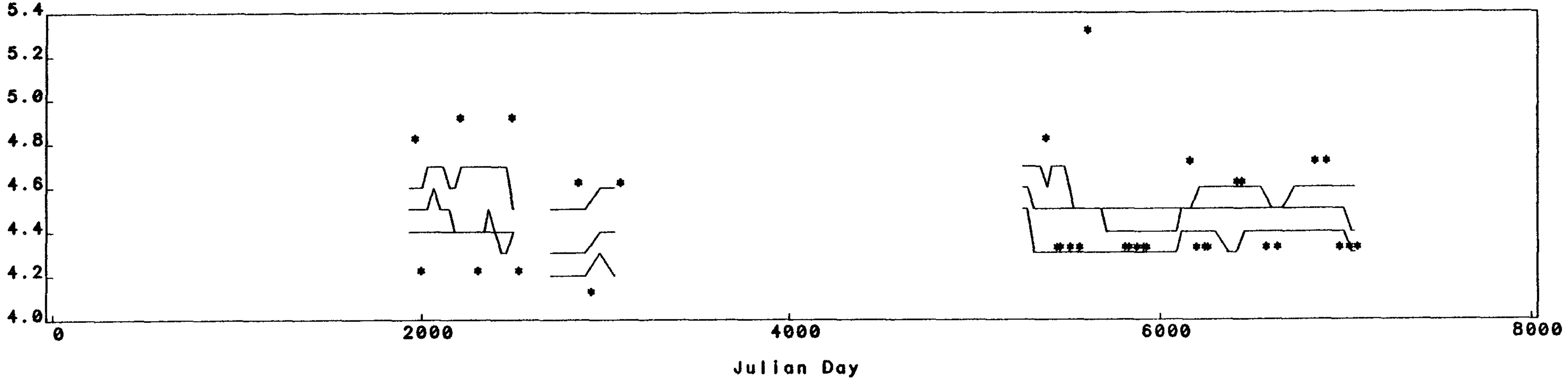


River no 11 pH +/- 6 months



River no 12 pH +/- 6 months

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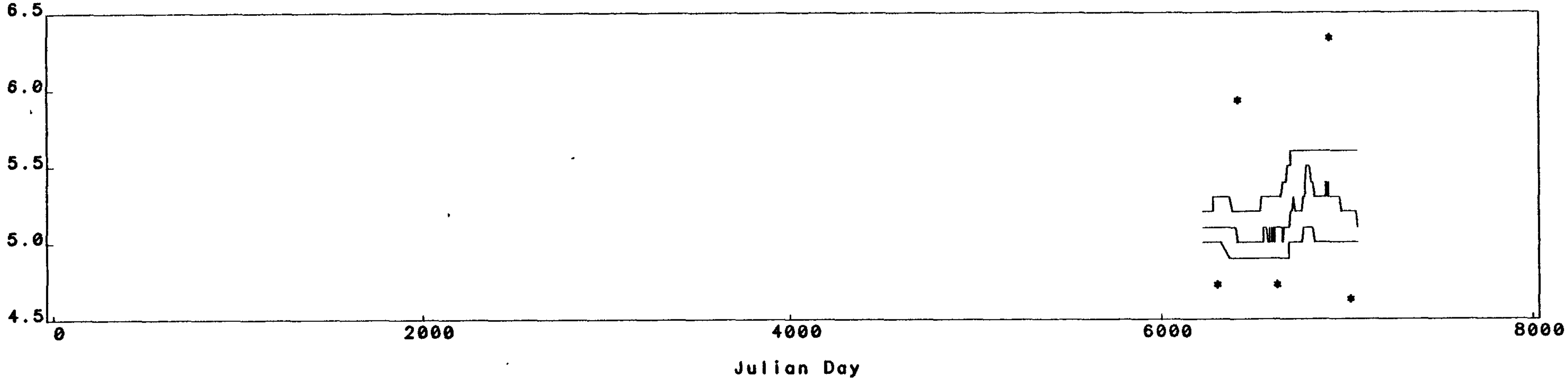
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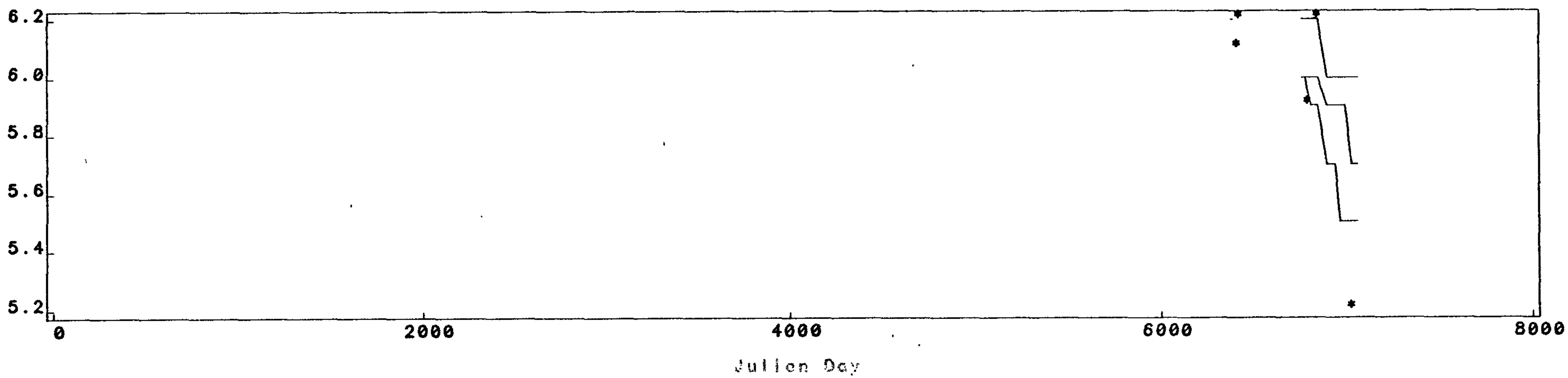
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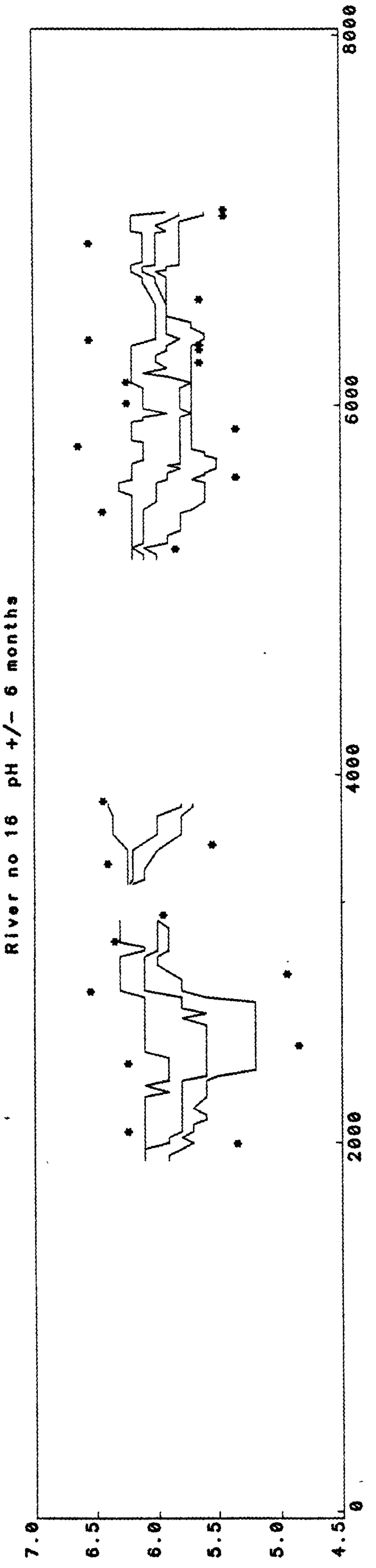
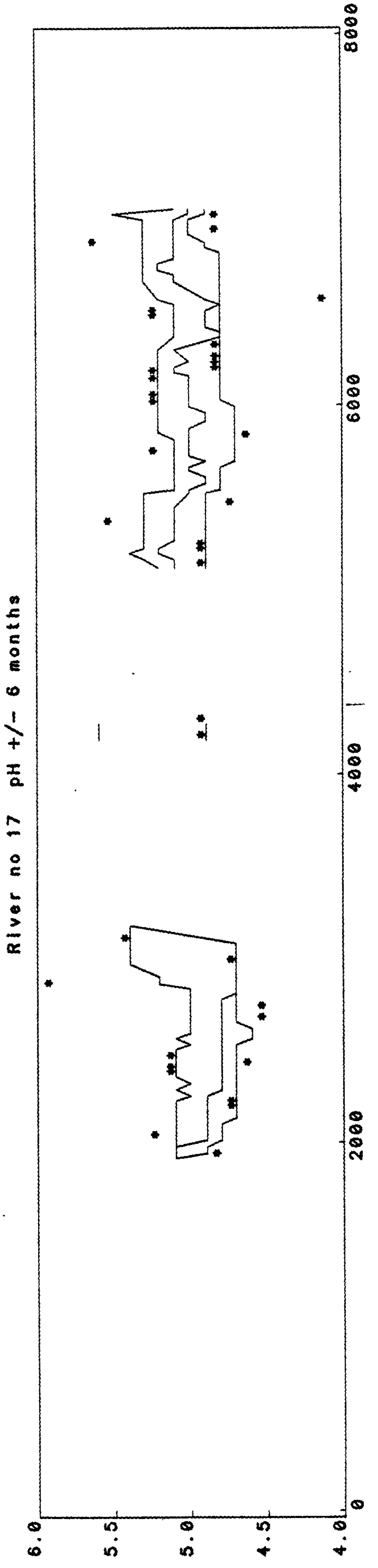
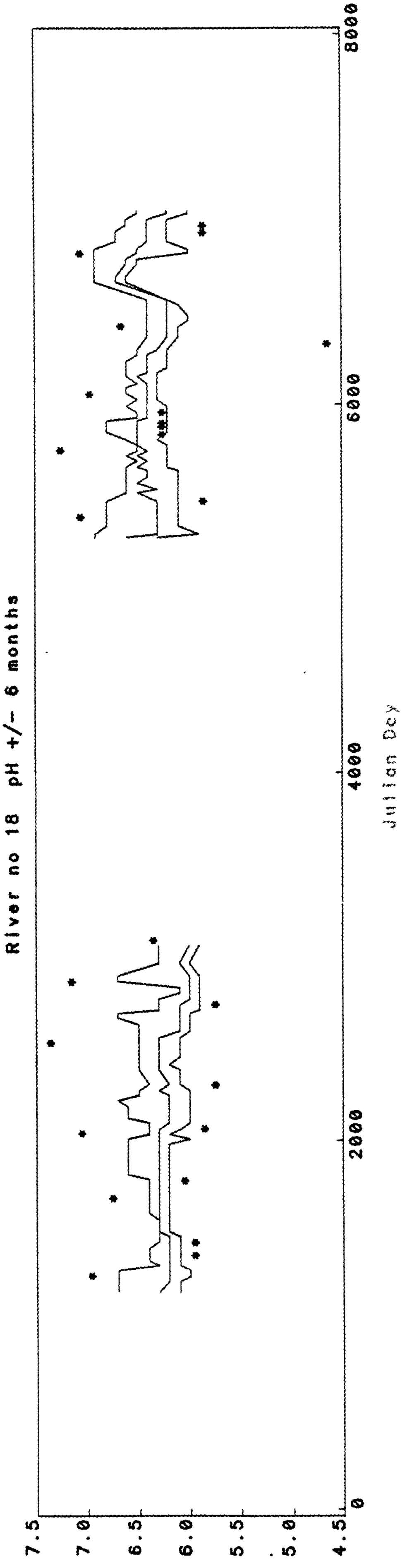

River no 16 pH +/- 6 months


River no 17 pH +/- 6 months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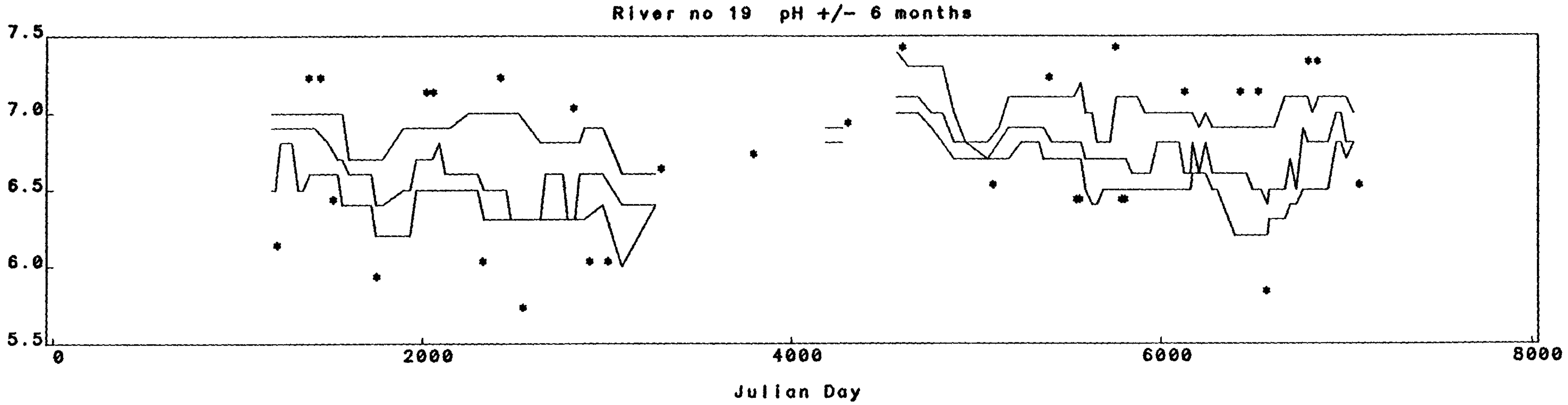
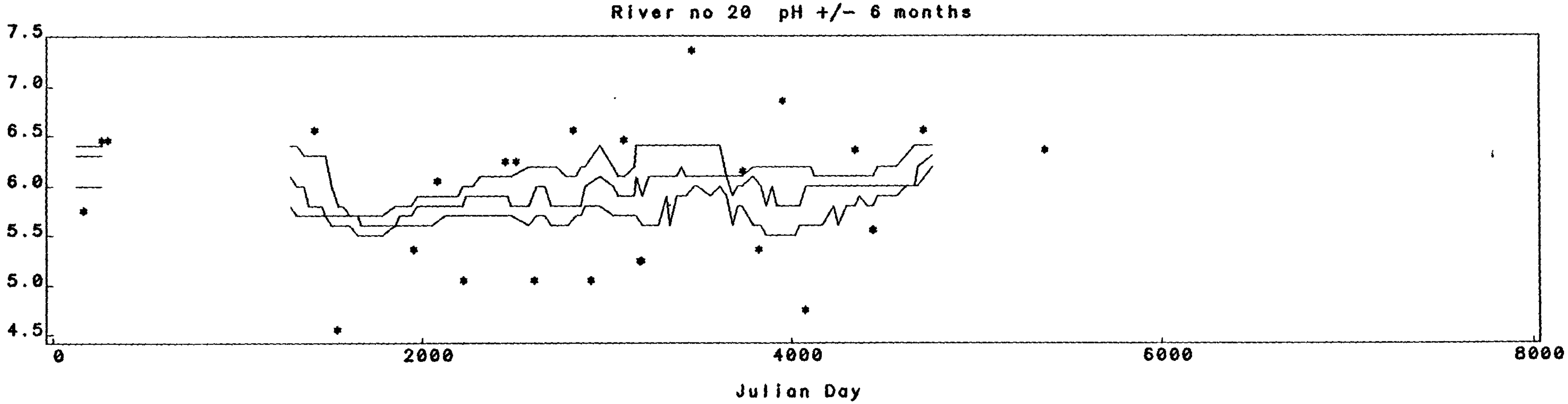
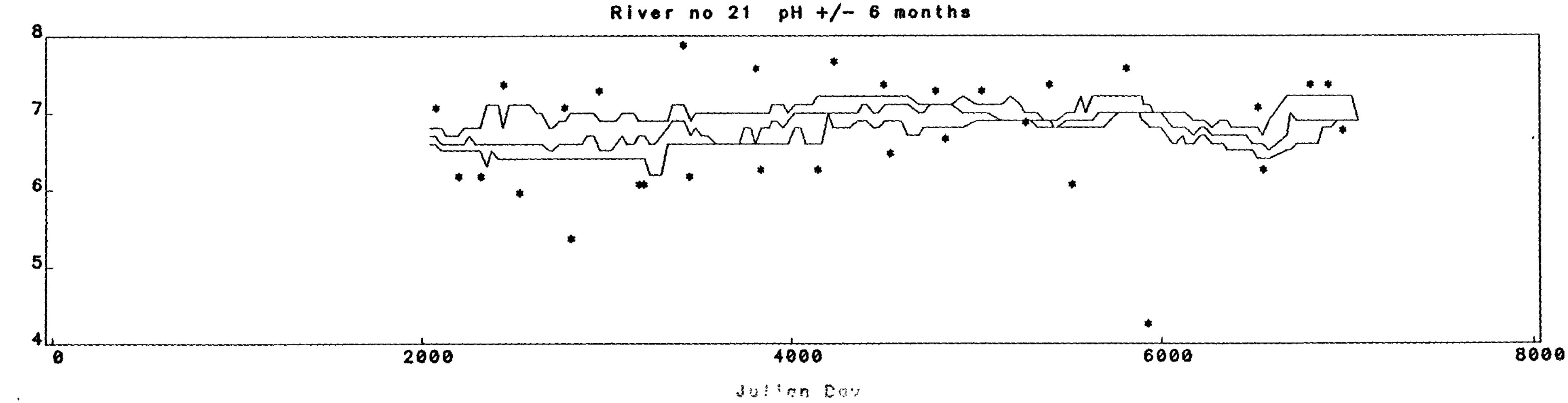
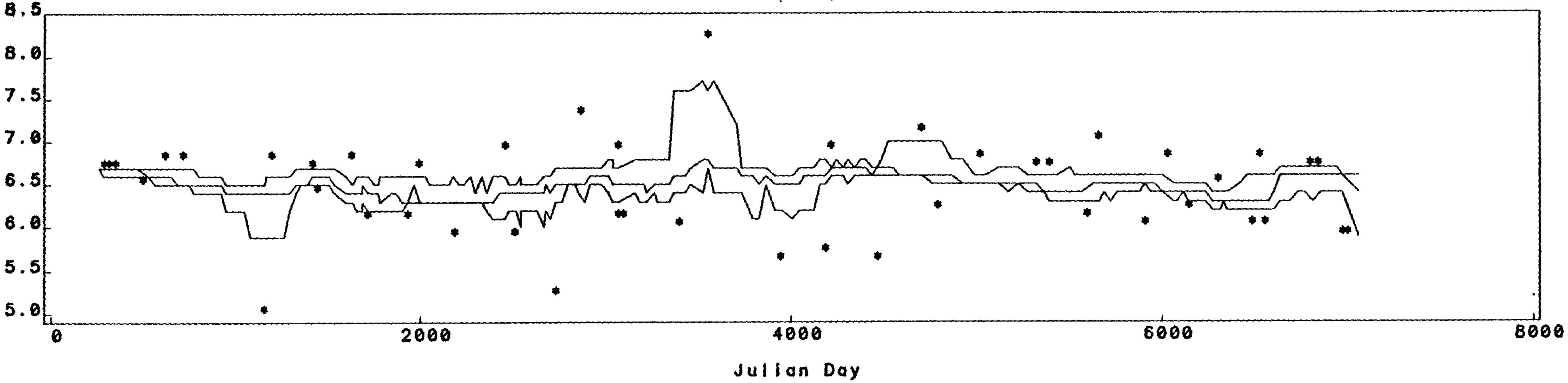

River no 19 pH +/- 6 months

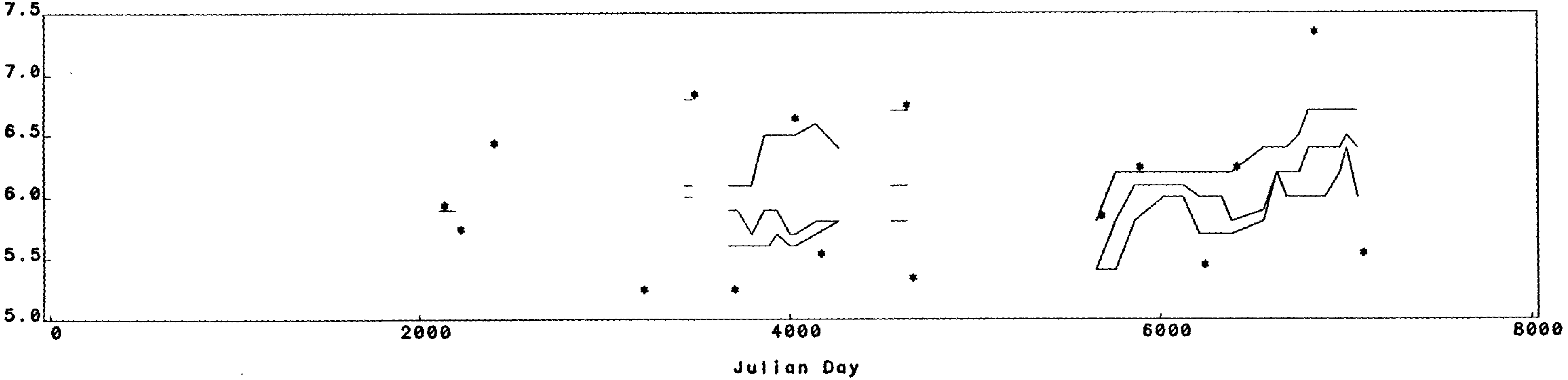

River no 20 pH +/- 6 months


River no 21 pH +/- 6 months

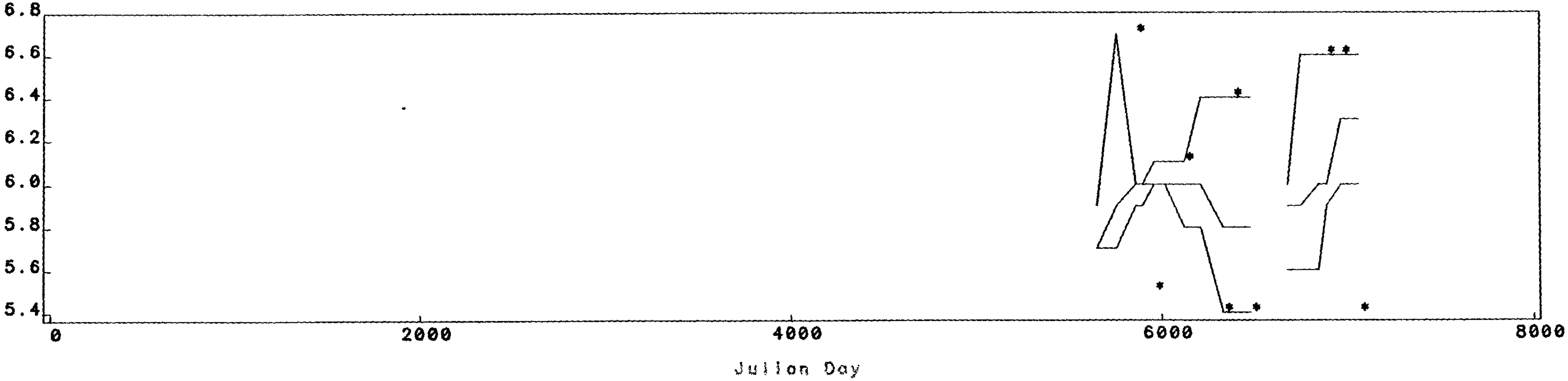
River no 22 pH +/- 6 months



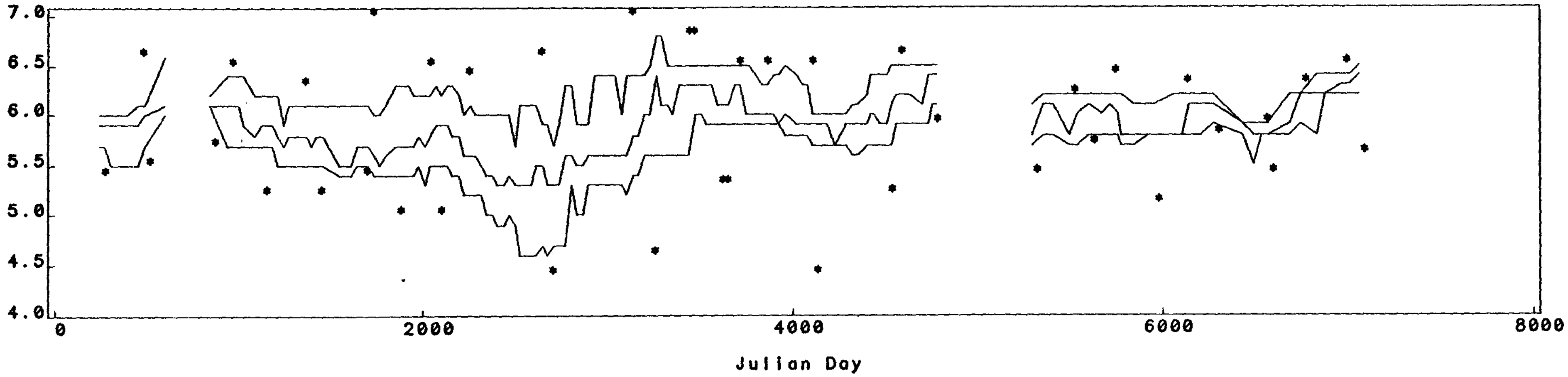
River no 23 pH +/- 6 months



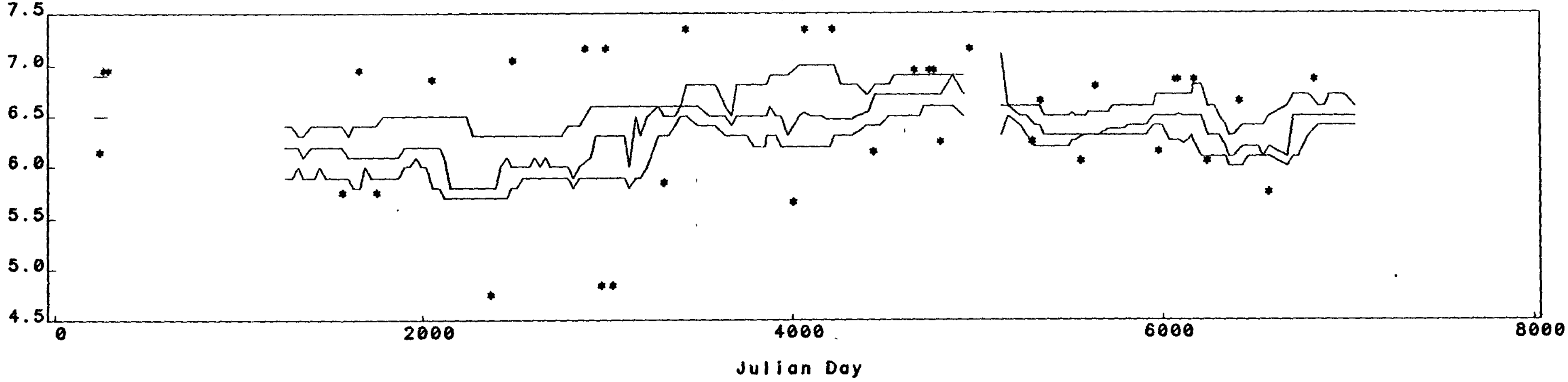
River no 24 pH +/- 6 months



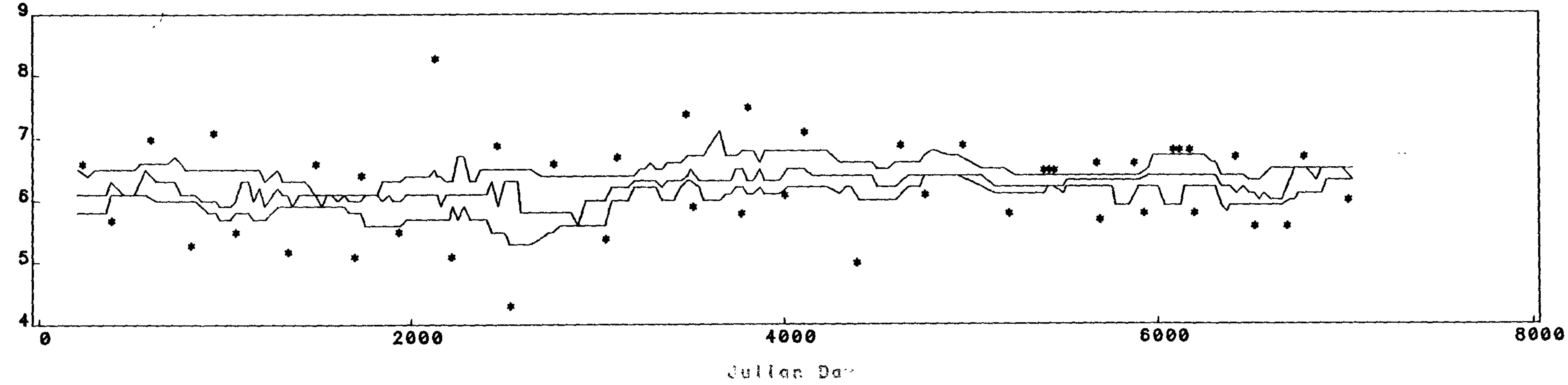
River no 25 pH +/- 6 months



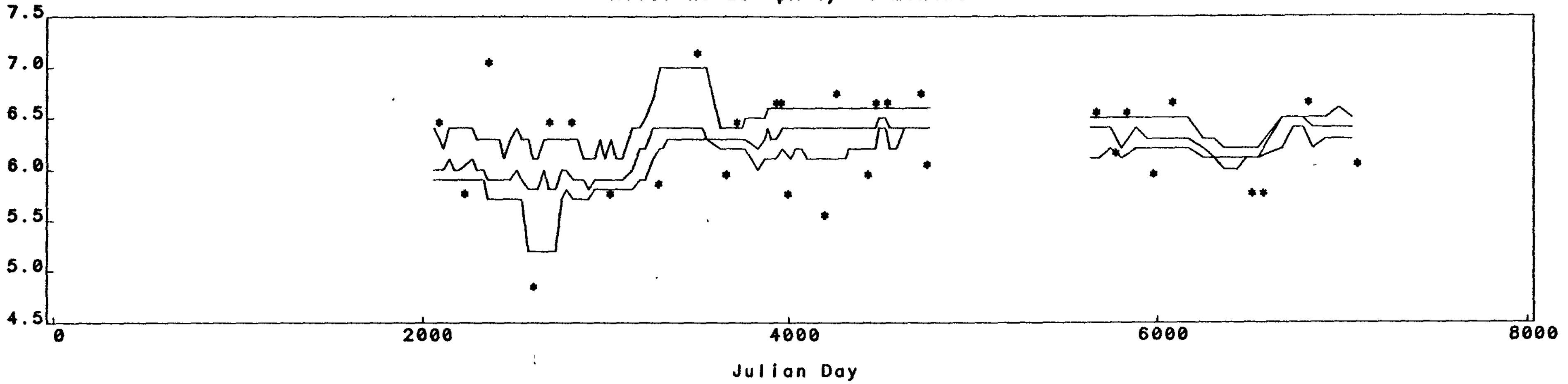
River no 26 pH +/- 6 months

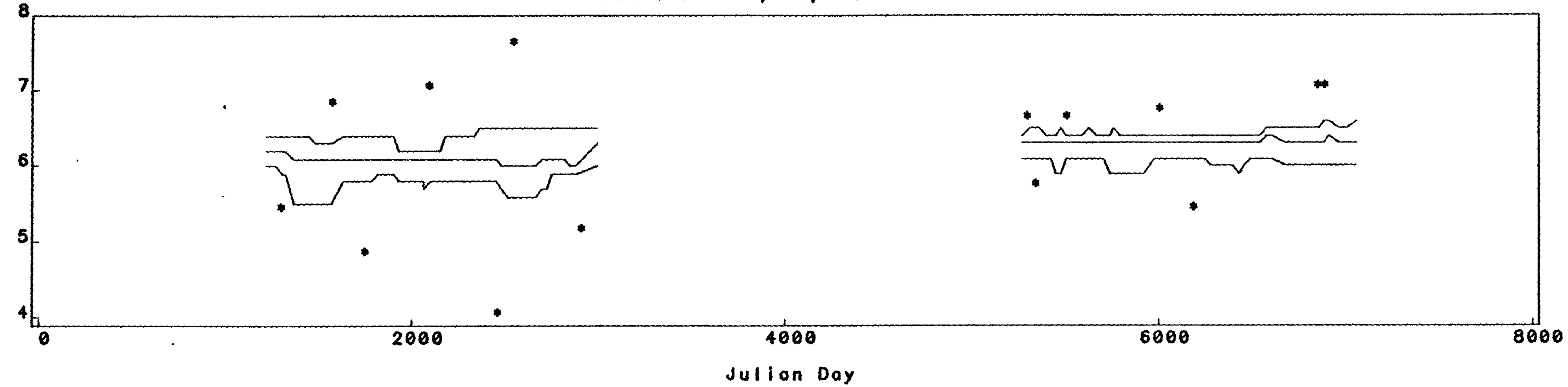


River no 27 pH +/- 6 months

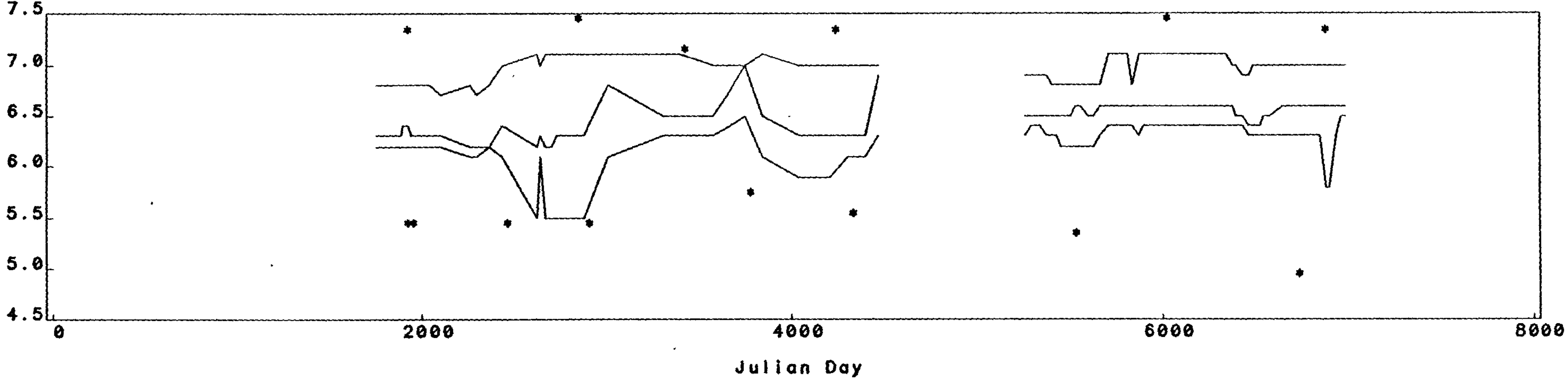


River no 28 pH +/- 6 months

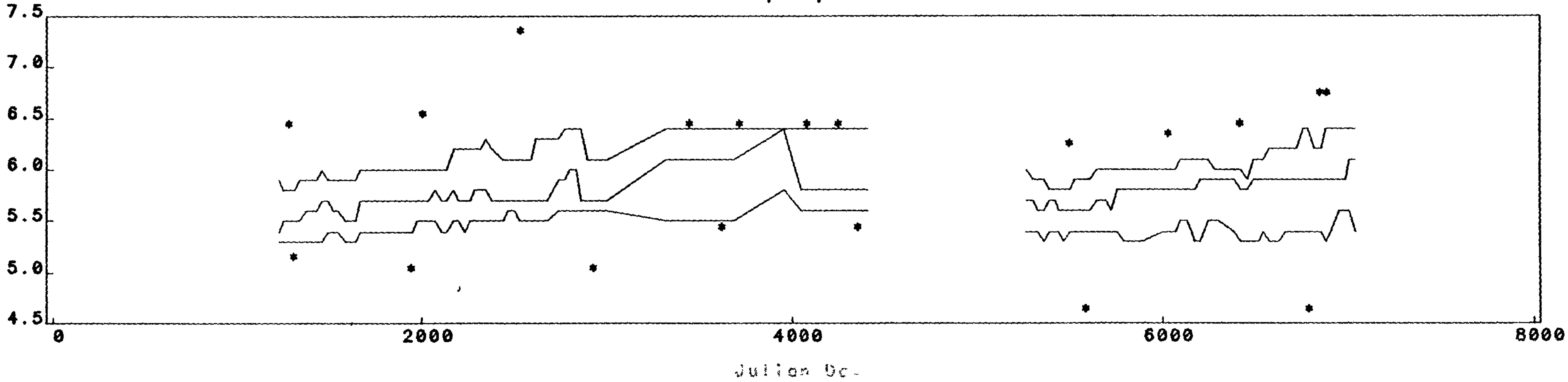




River no 1 pH +/- 12 months

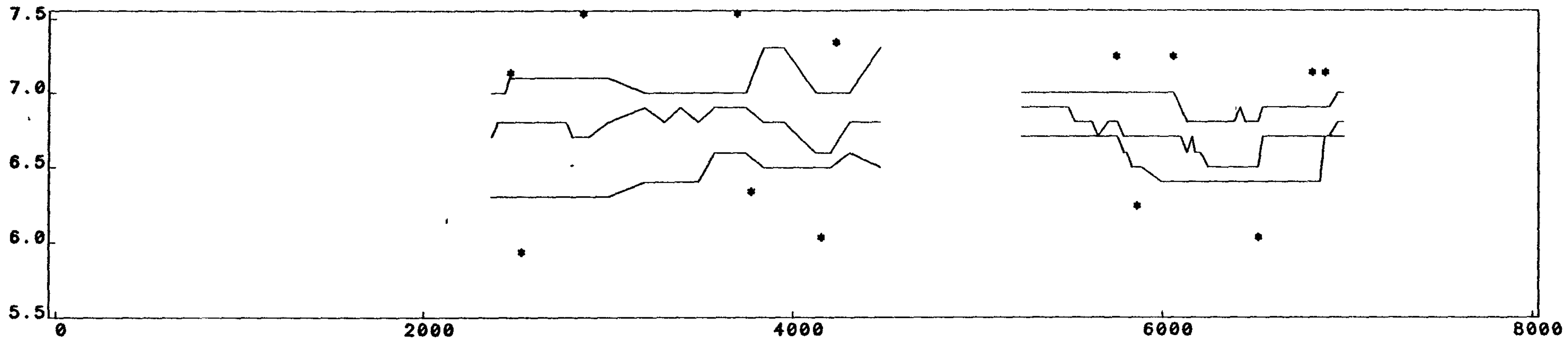


River no 2 pH +/- 12 months

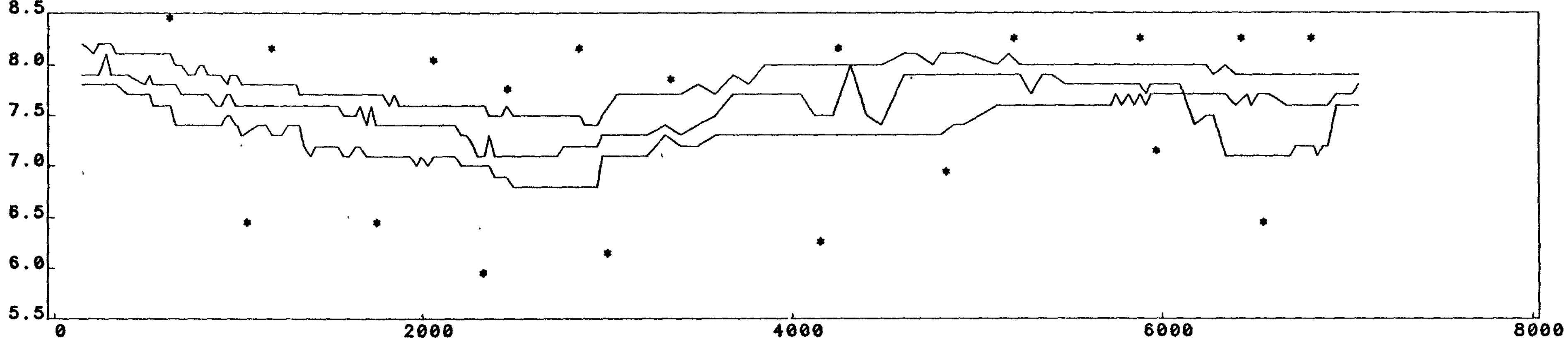


River no 3 pH +/- 12 months

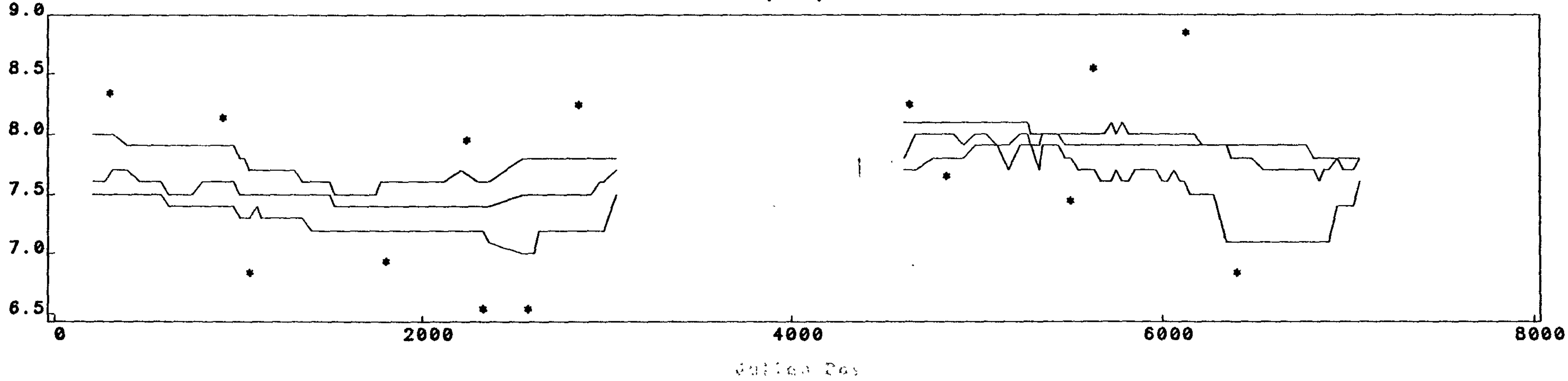
River no 4 pH +/- 12 months



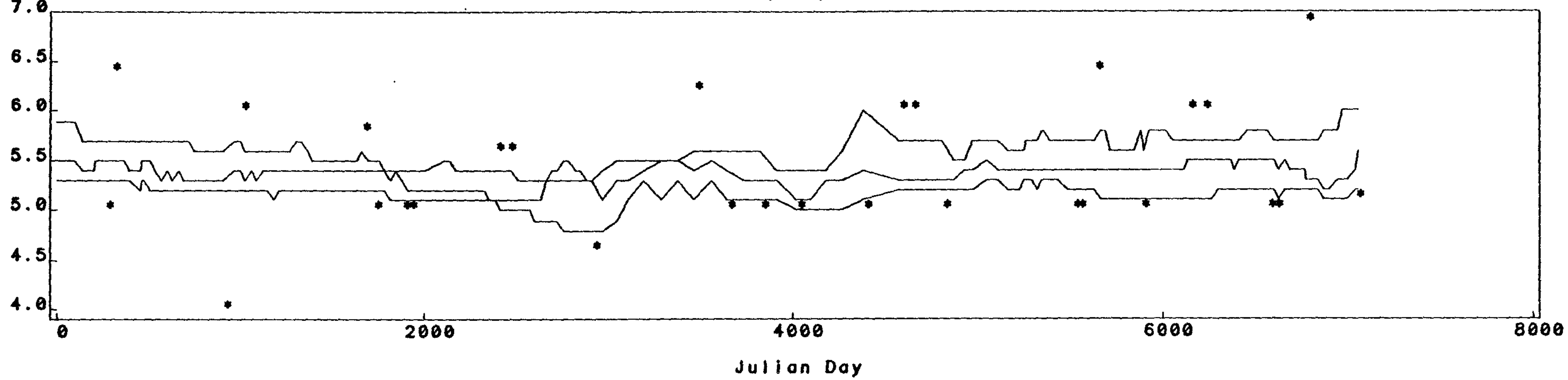
River no 5 pH +/- 12 months



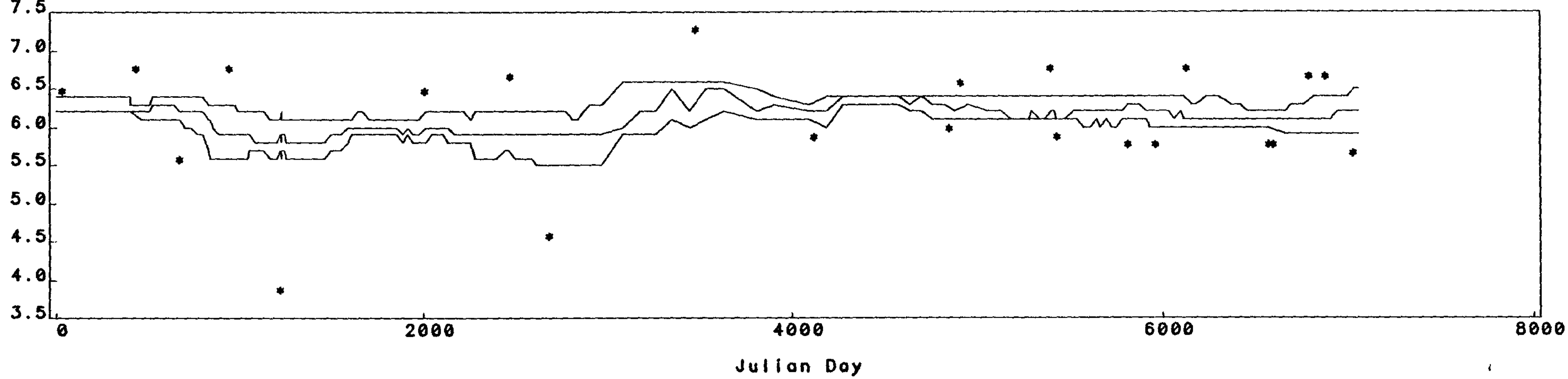
River no 6 pH +/- 12 months



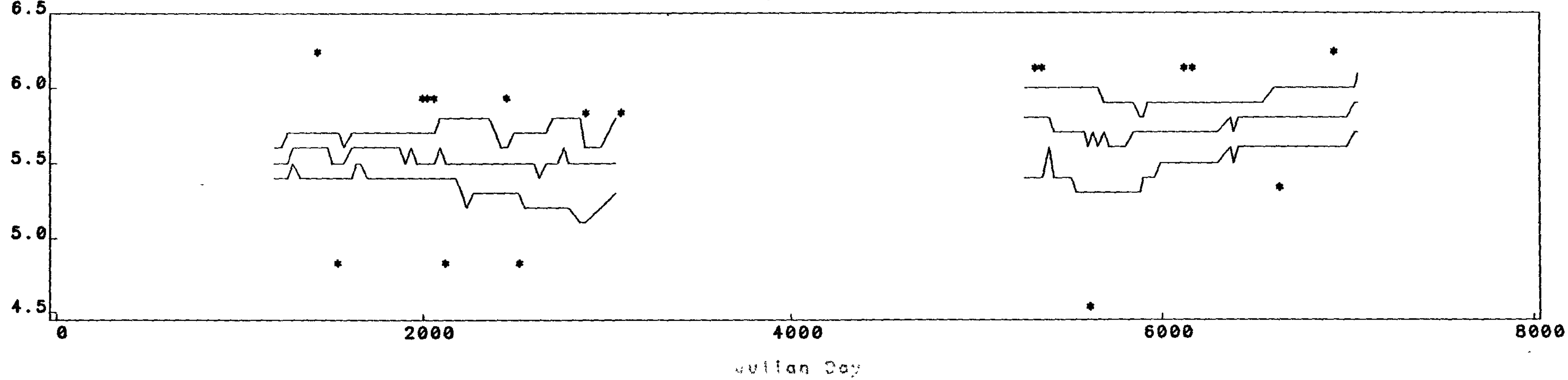
River no 7 pH +/- 12 months



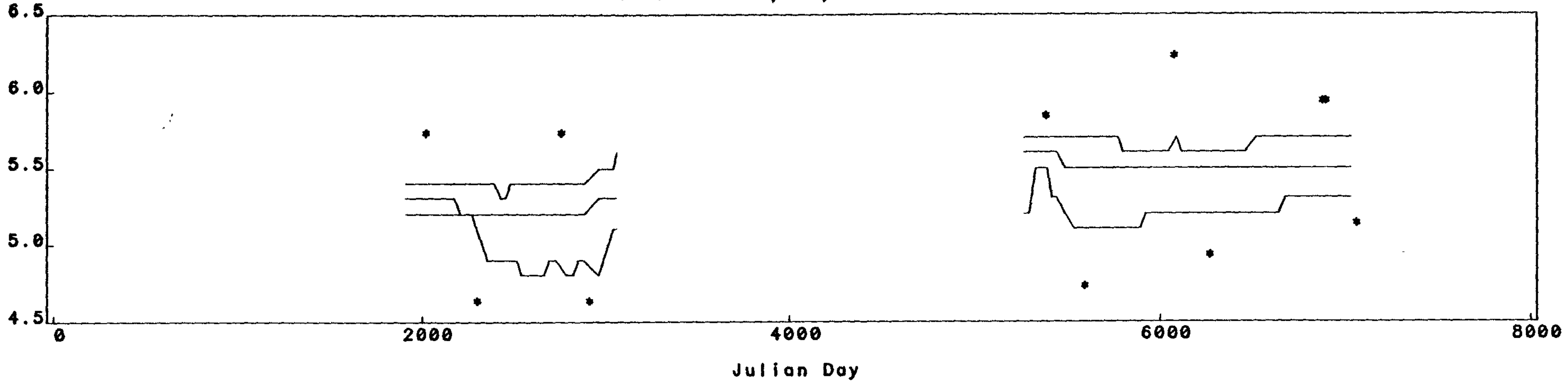
River no 8 pH +/- 12 months



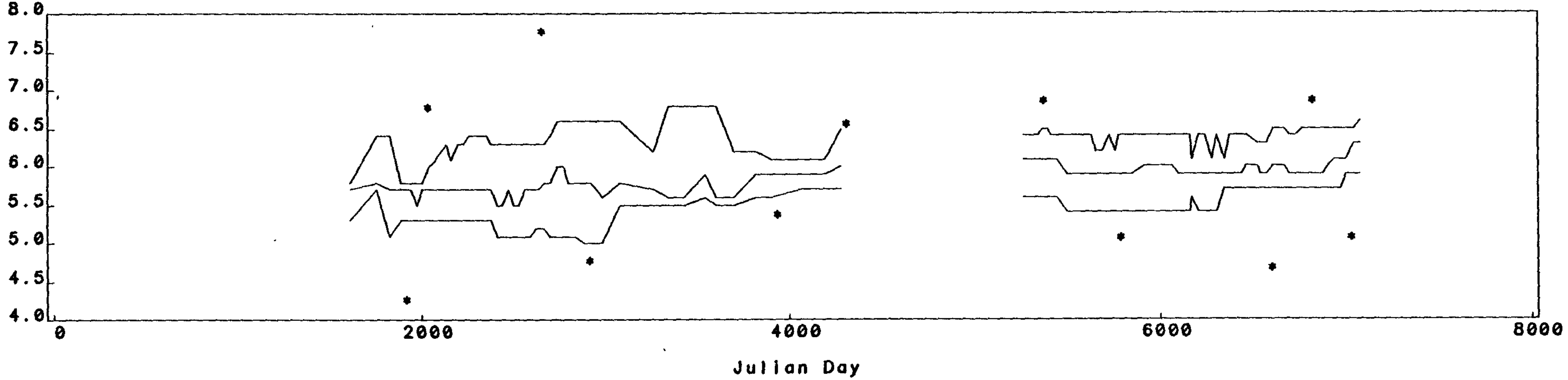
River no 9 pH +/- 12 months



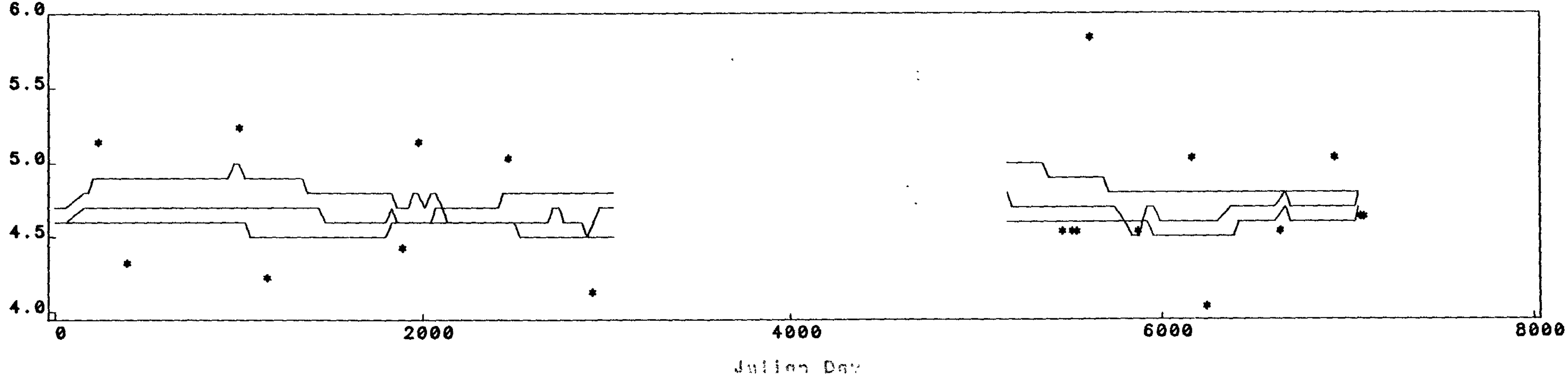
River no 10 pH +/- 12 months



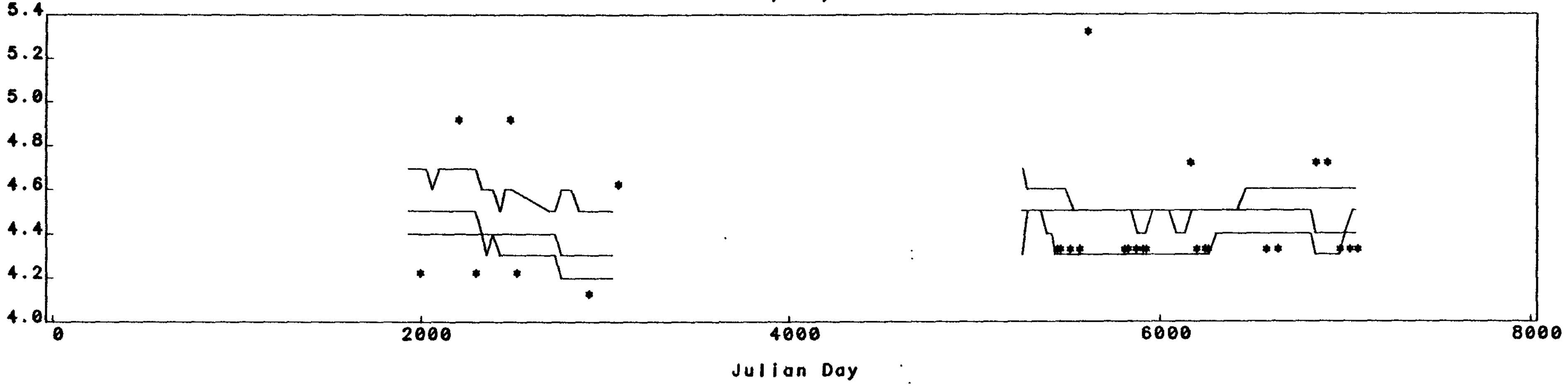
River no 11 pH +/- 12 months



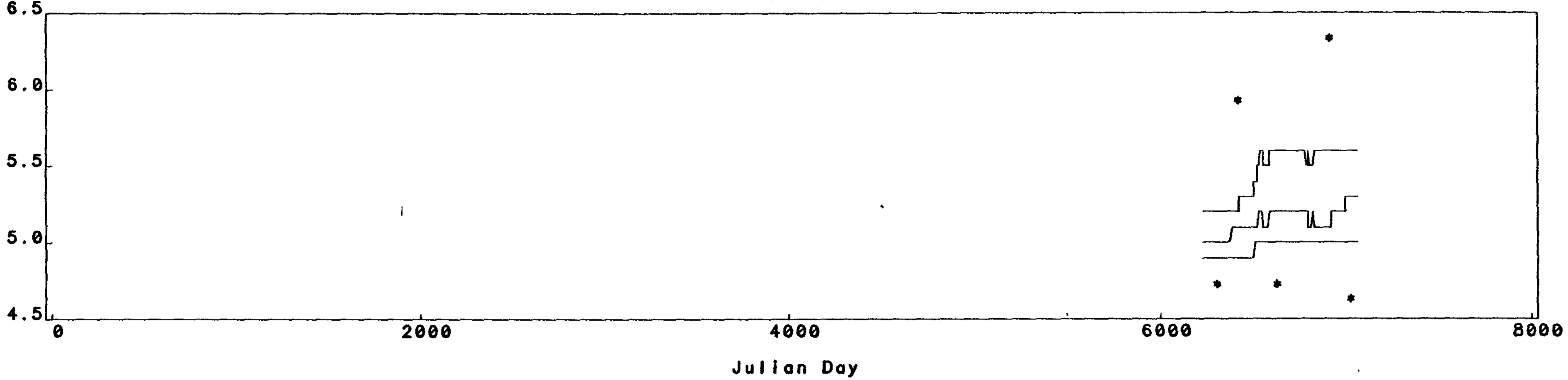
River no 12 pH +/- 12 months



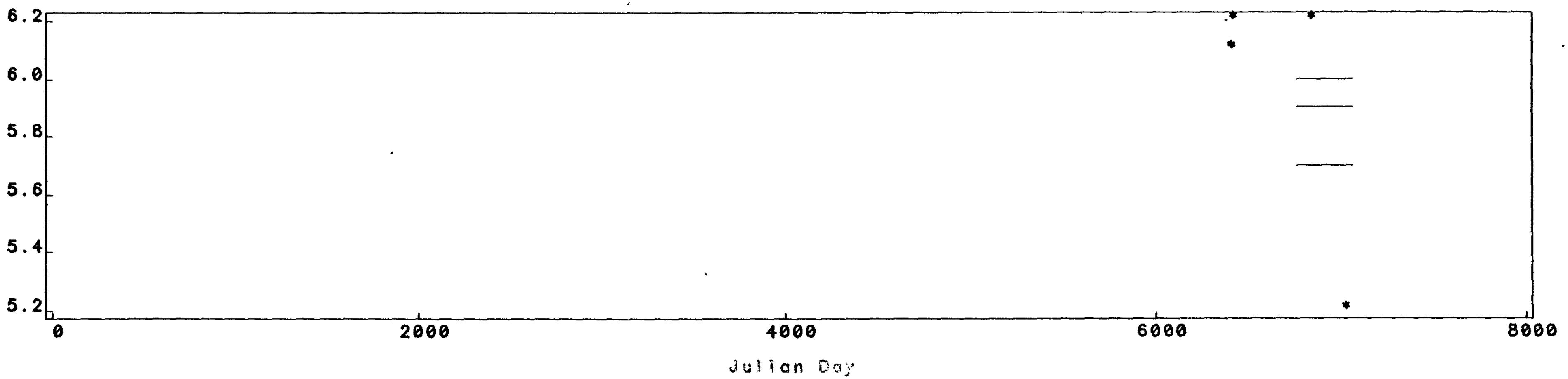
River no 13 pH +/- 12 months

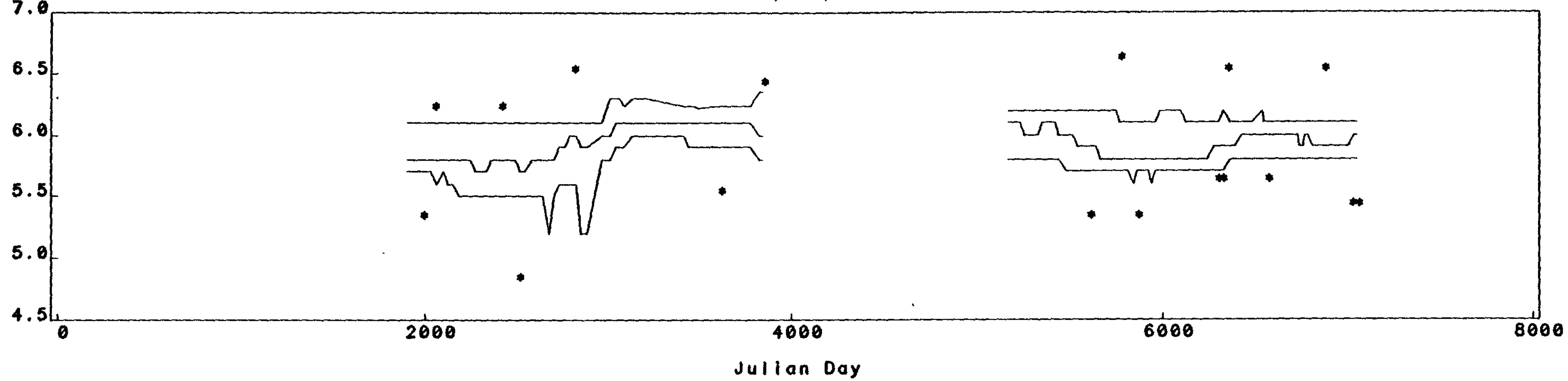


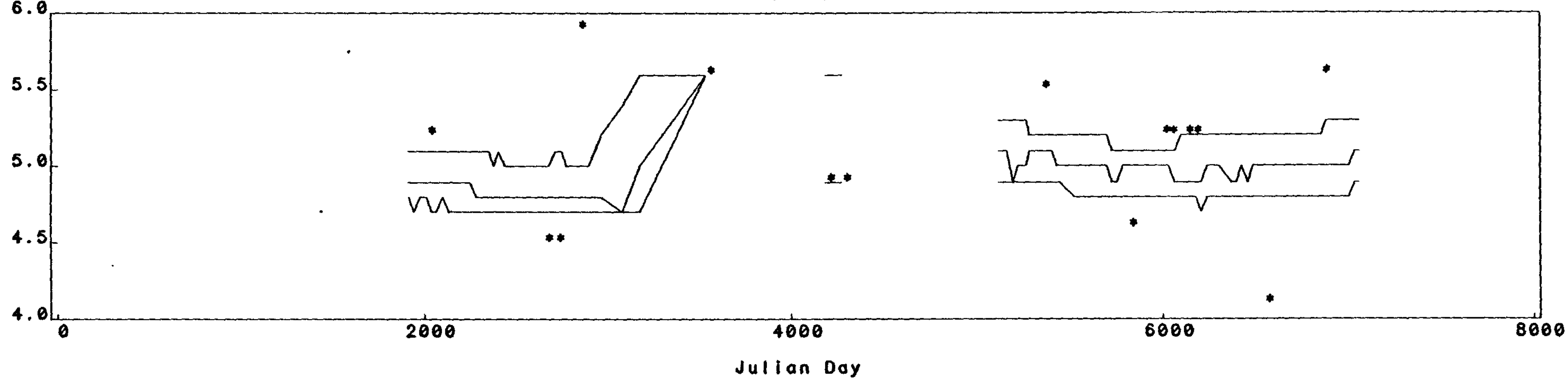
River no 14 pH +/- 12 months

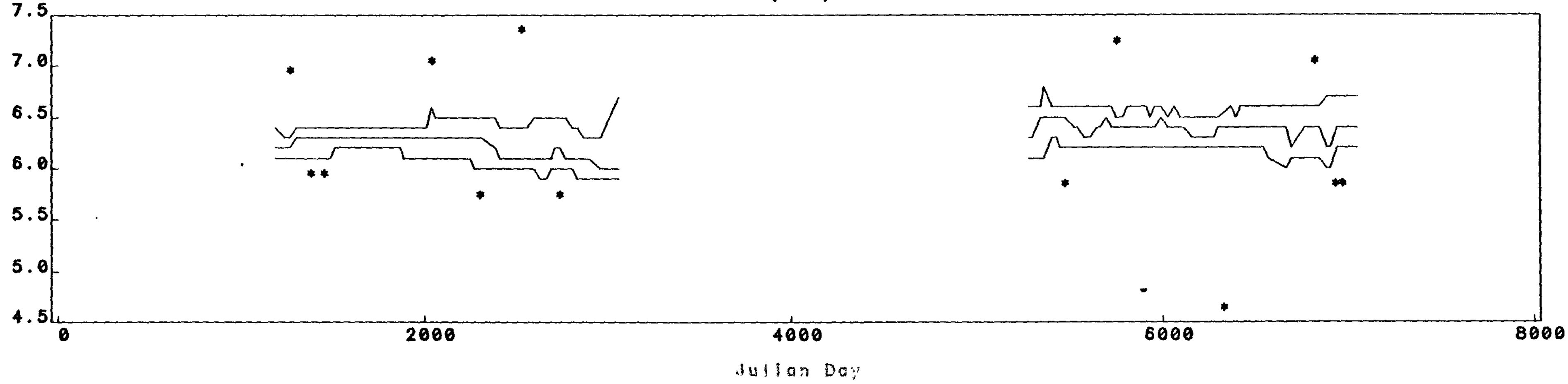


River no 15 pH +/- 12 months

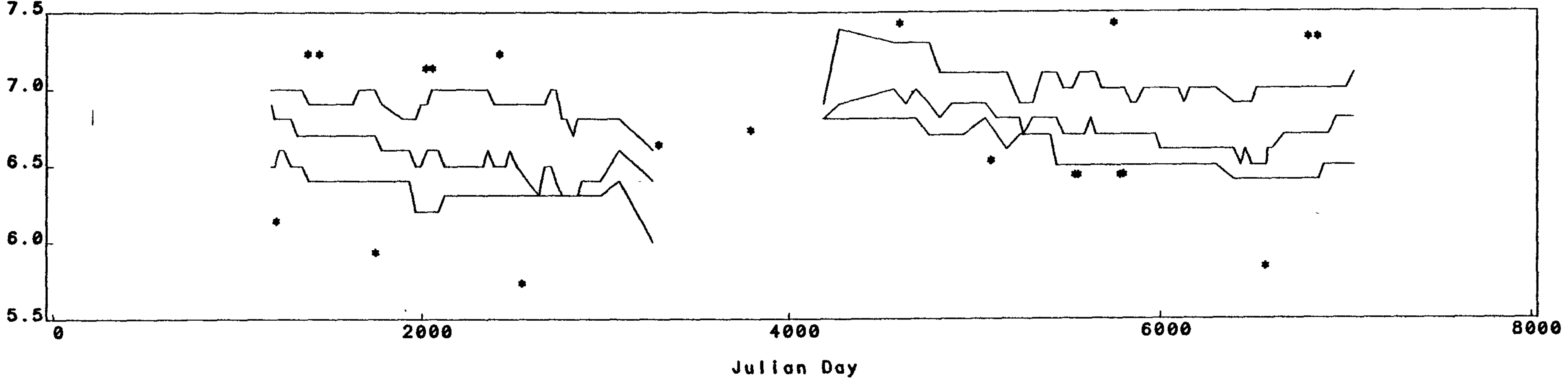



River no 16 pH +/- 12 months

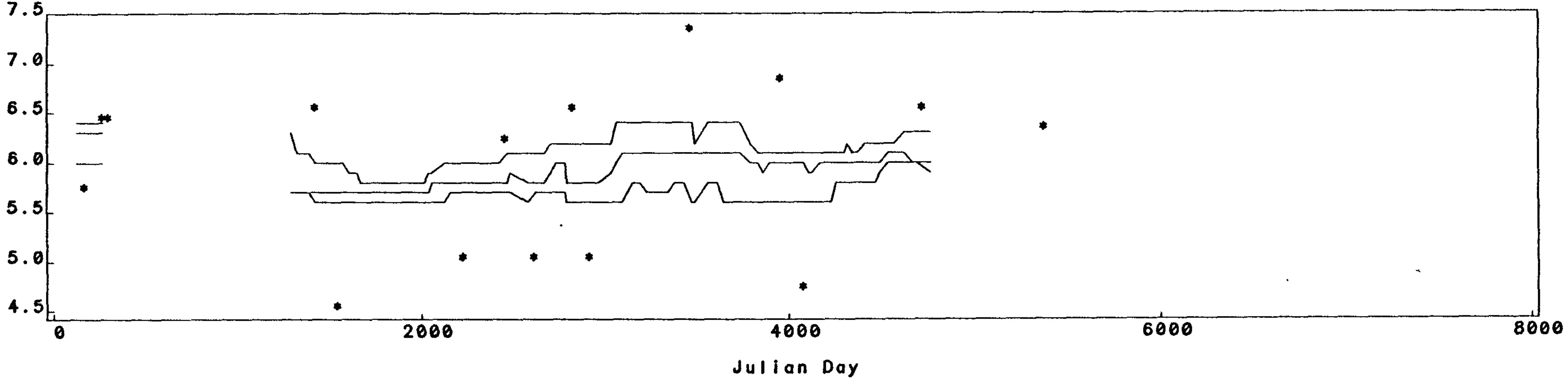

River no 17 pH +/- 12 months


River no 18 pH +/- 12 months

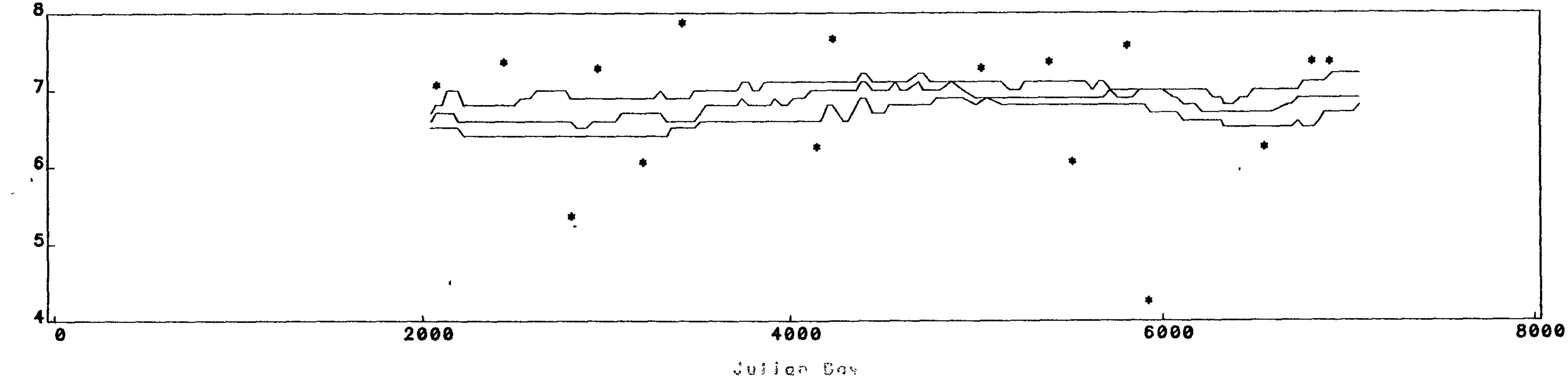
River no 19 pH +/- 12 months



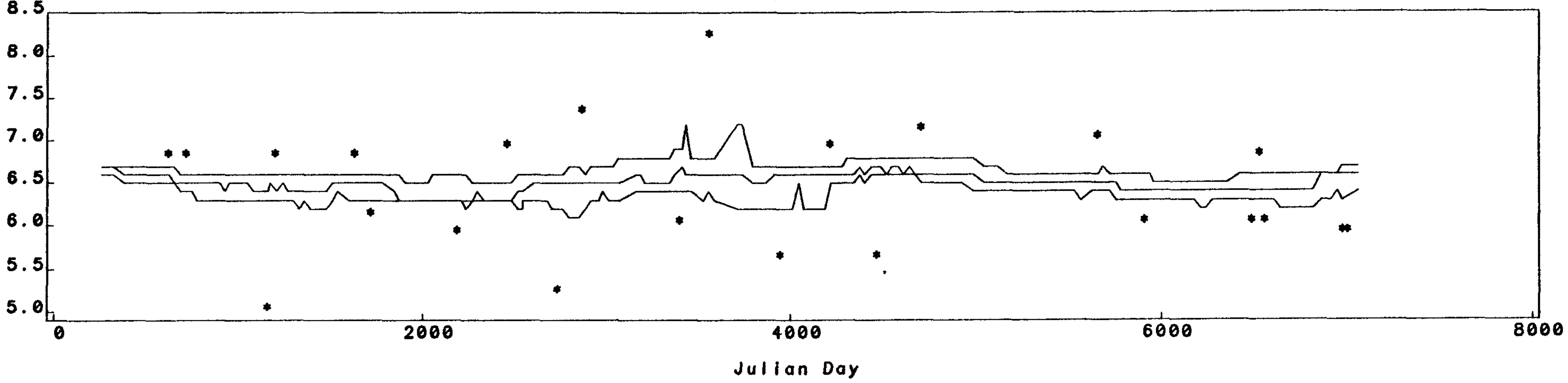
River no 20 pH +/- 12 months



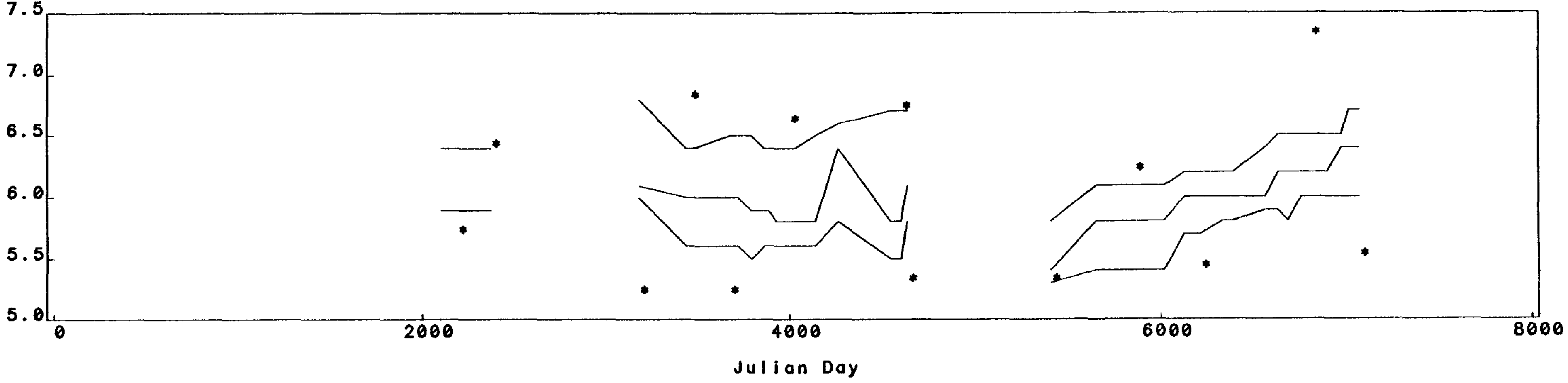
River no 21 pH +/- 12 months



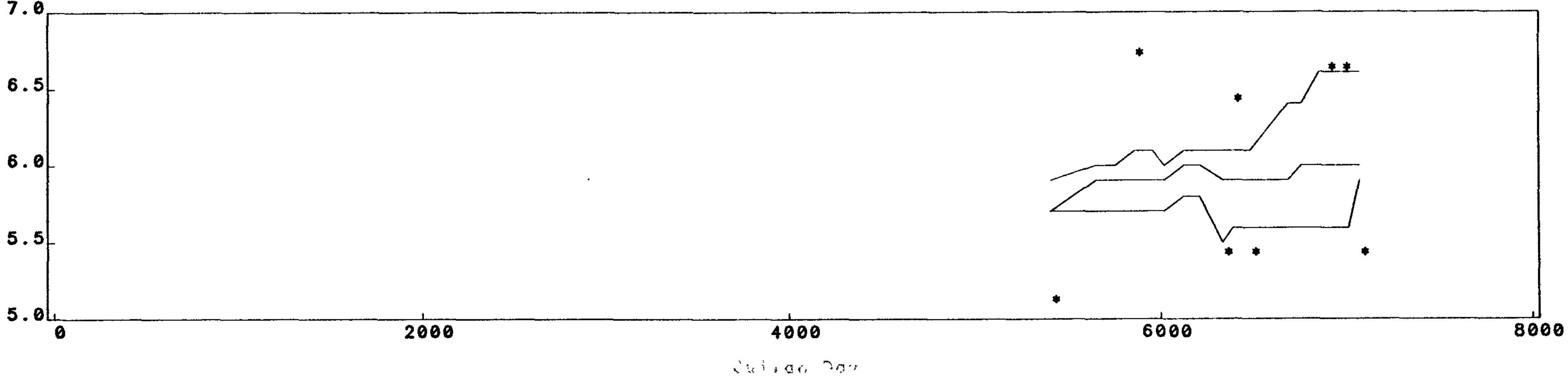
River no 22 pH +/- 12 months



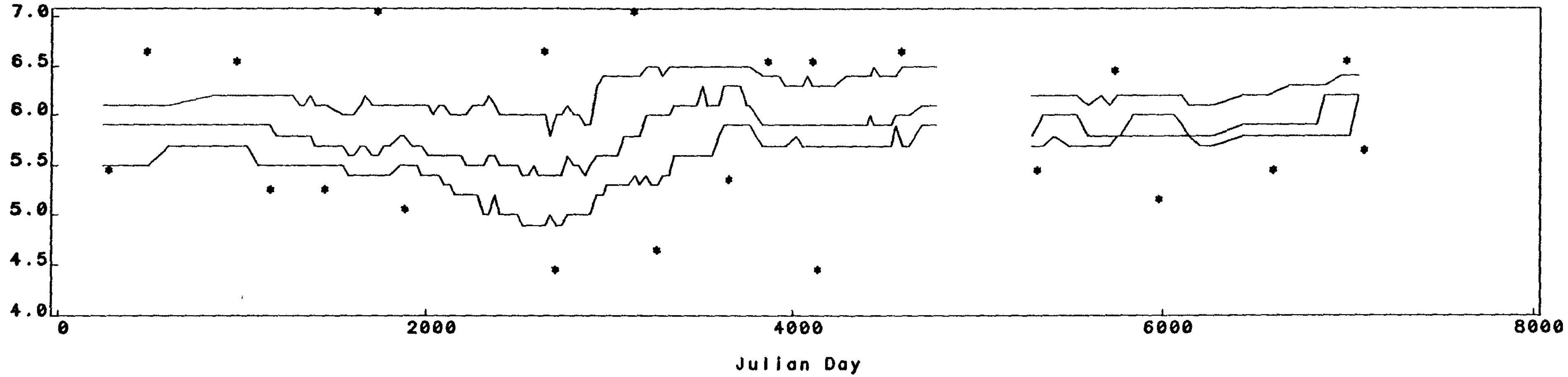
River no 23 pH +/- 12 months



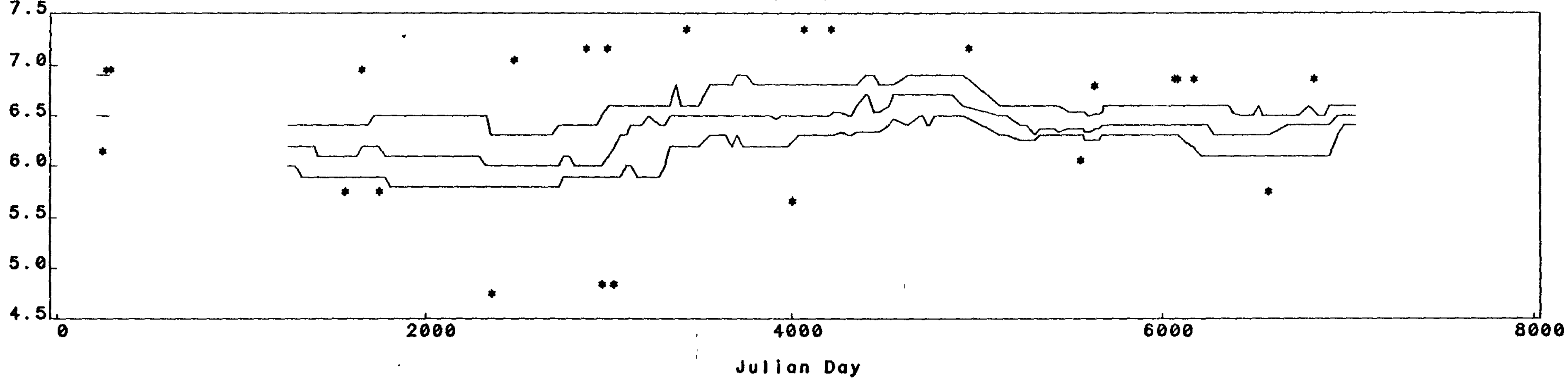
River no 24 pH +/- 12 months



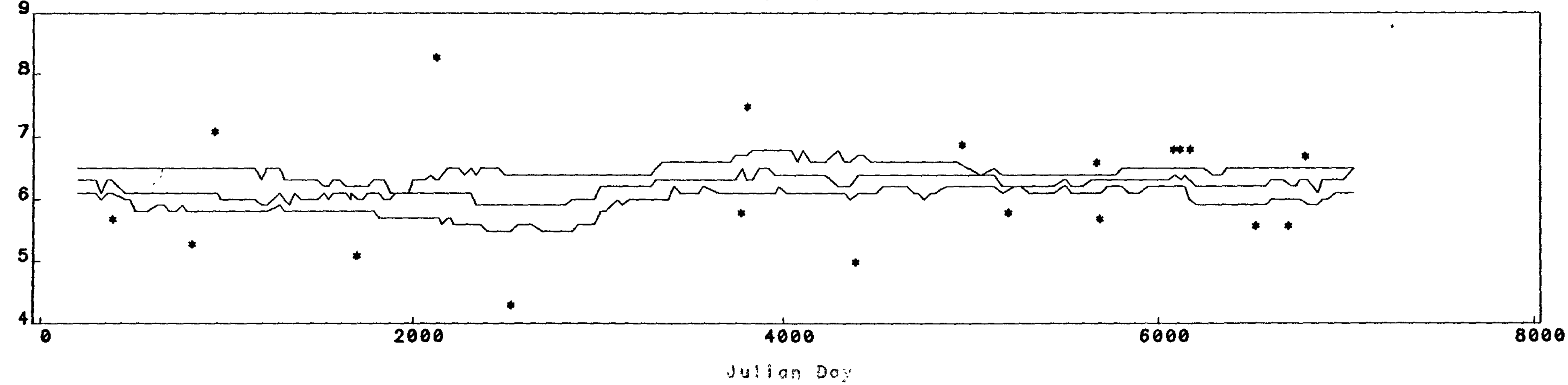
River no 25 pH +/- 12 months



River no 26 pH +/- 12 months



River no 27 pH +/- 12 months



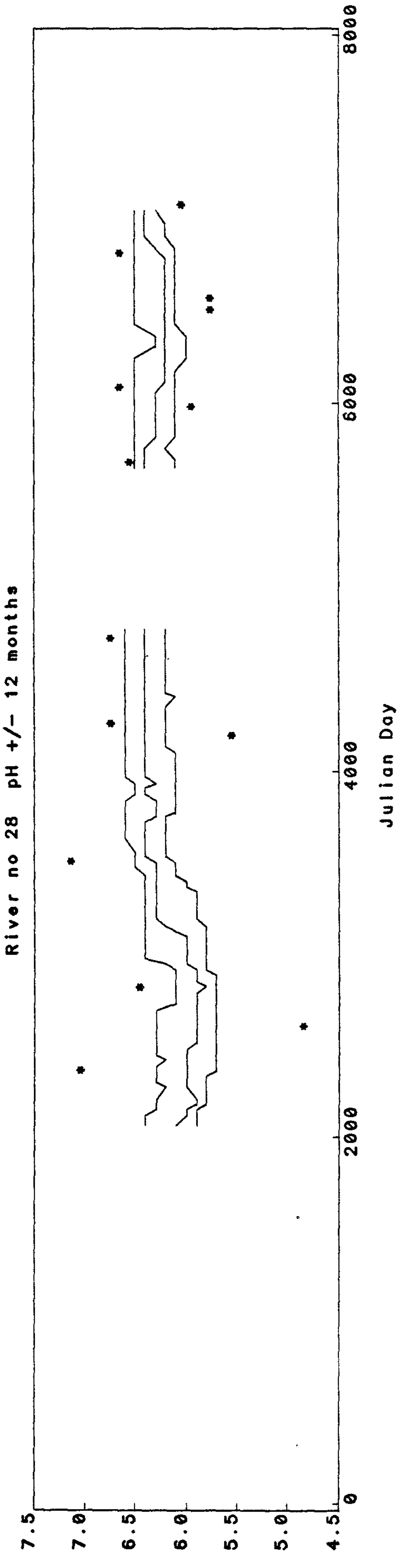
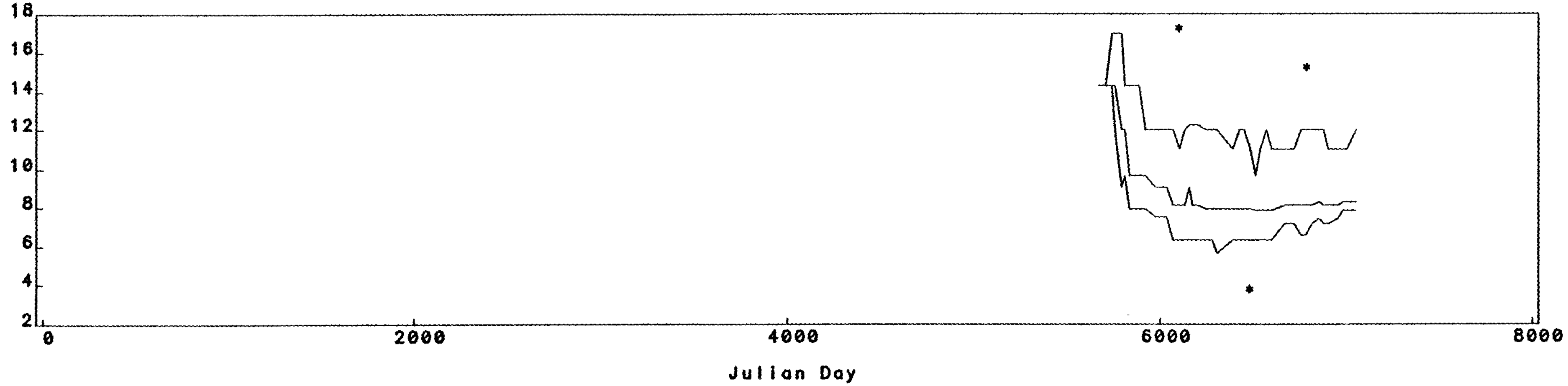
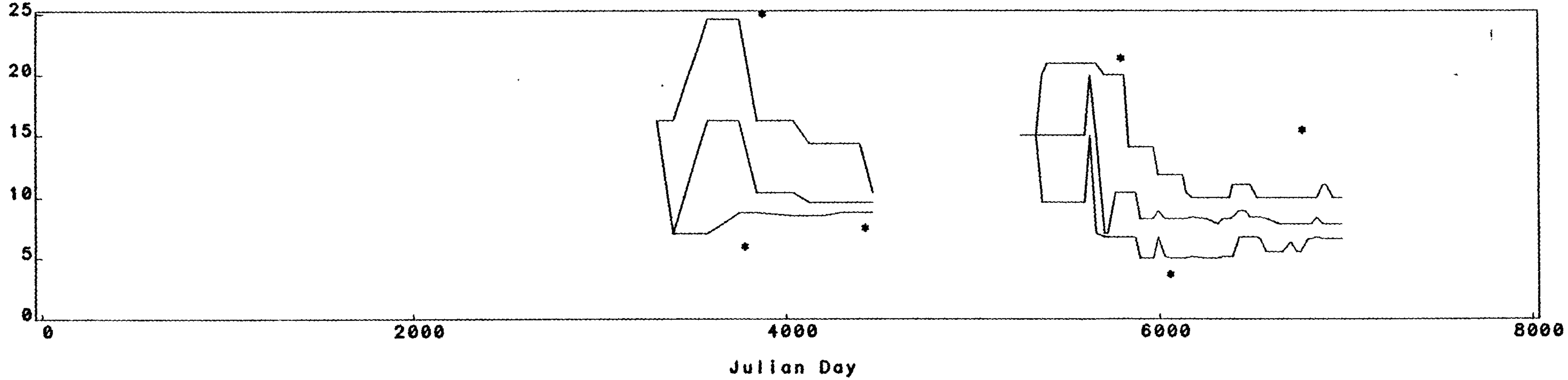
River no 28 pH +/- 12 months
Julian Day
0
2000
4000
6000
8000
4.5
5.0
5.5
6.0
6.5
7.0
7.5

Figure 9. Running boxplots of dissolved organic carbon for the study rivers.

River no 1 DOC



River no 2 DOC



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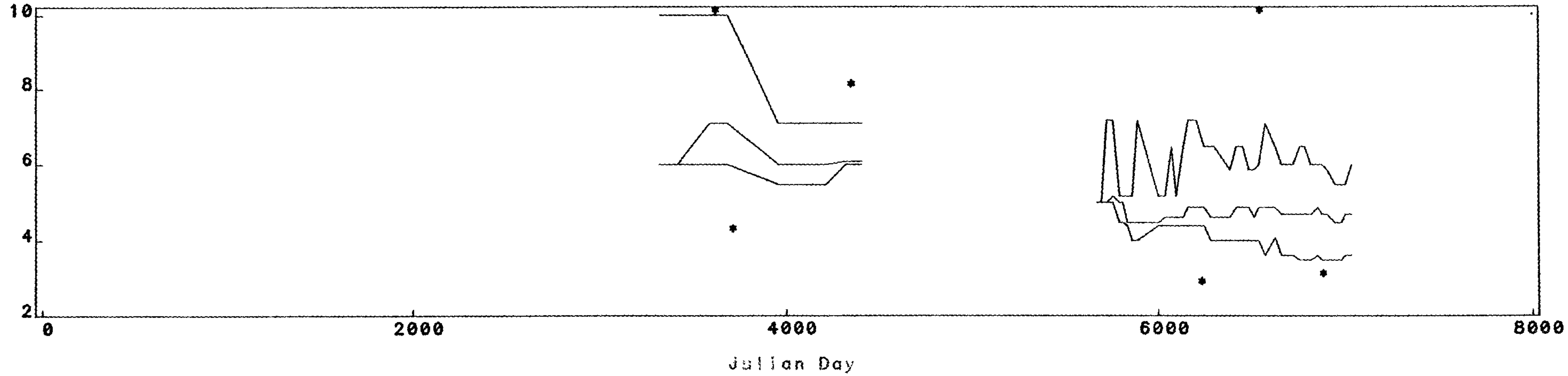

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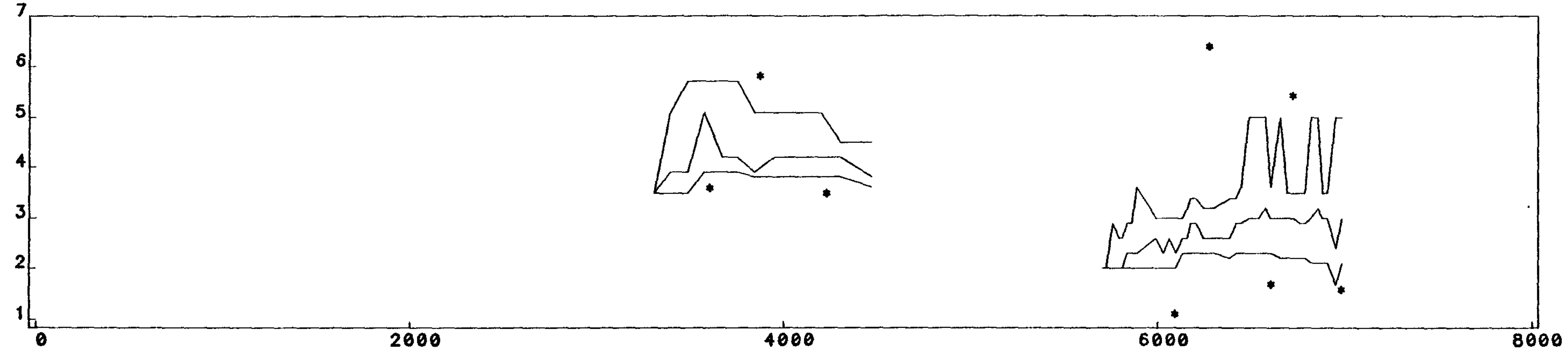

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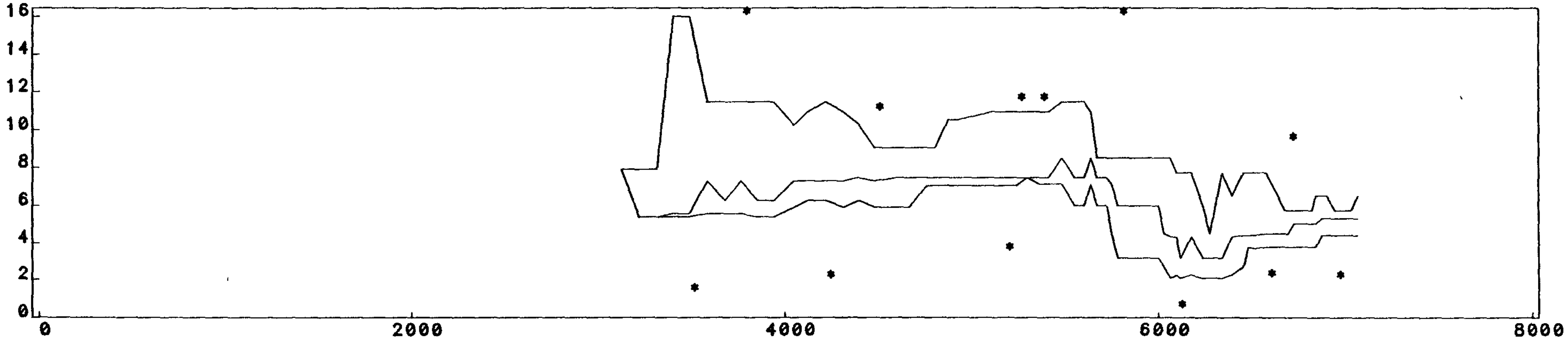

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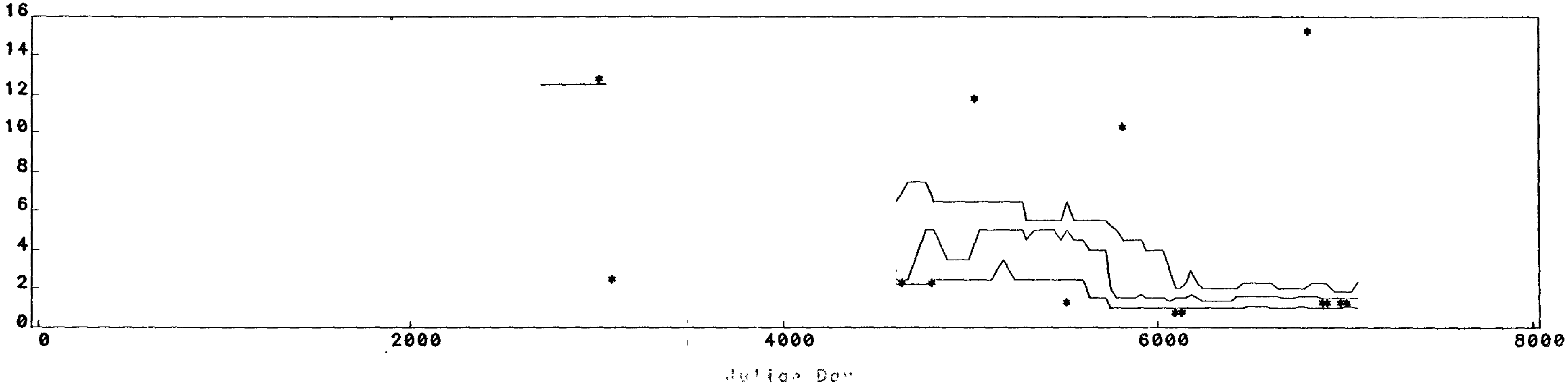

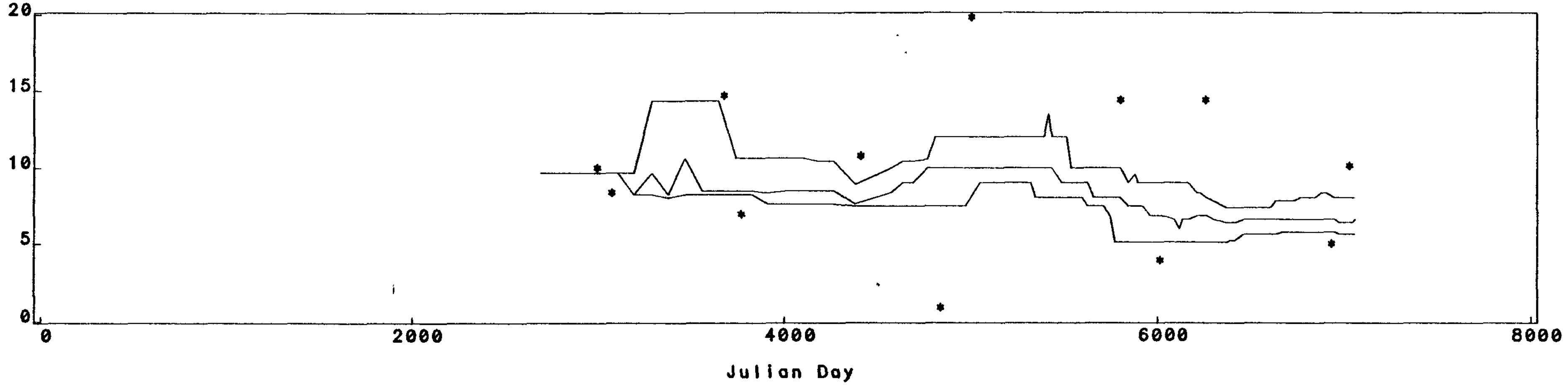
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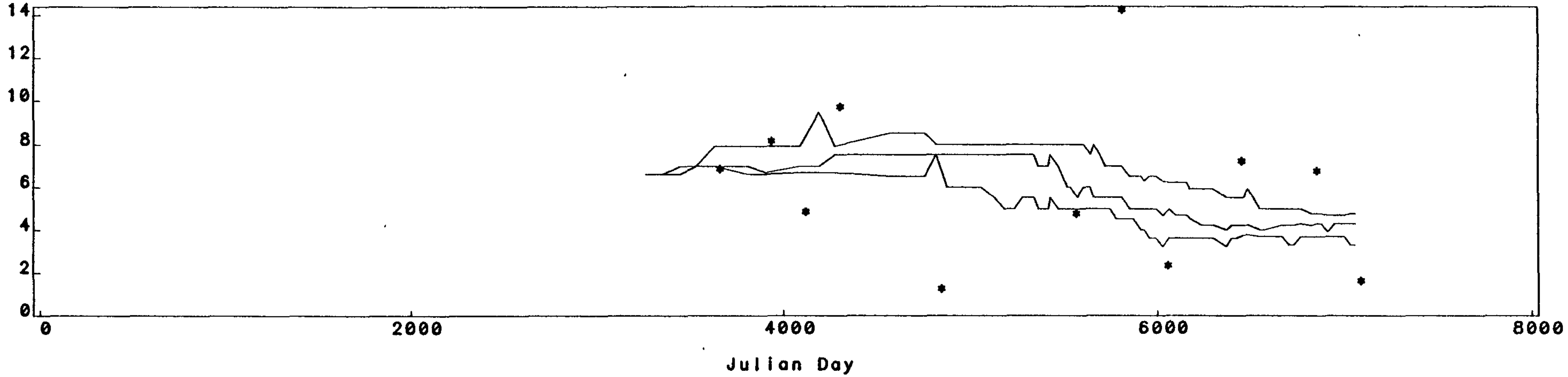
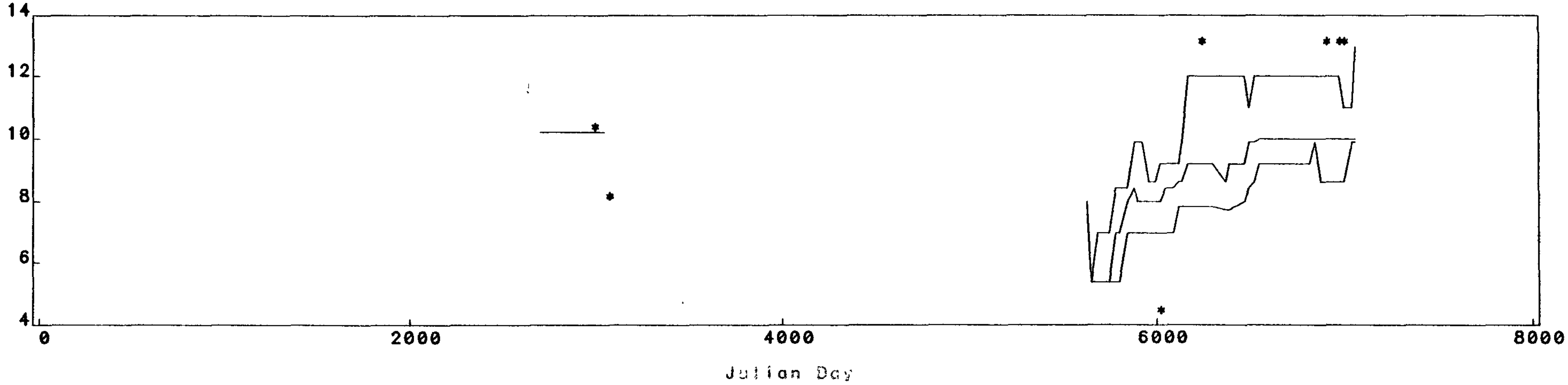
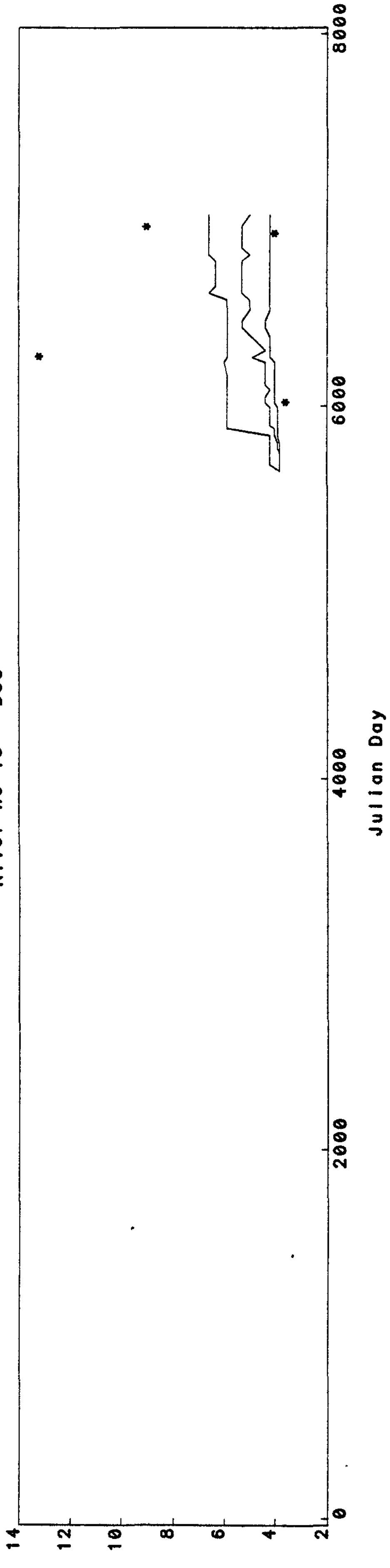
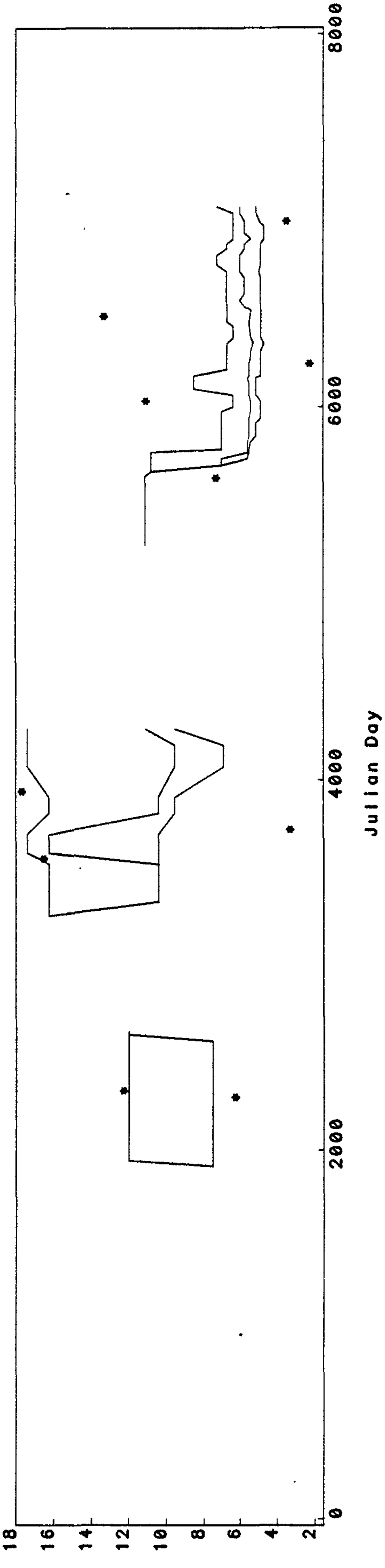

River no 8 DOC


River no 9 DOC

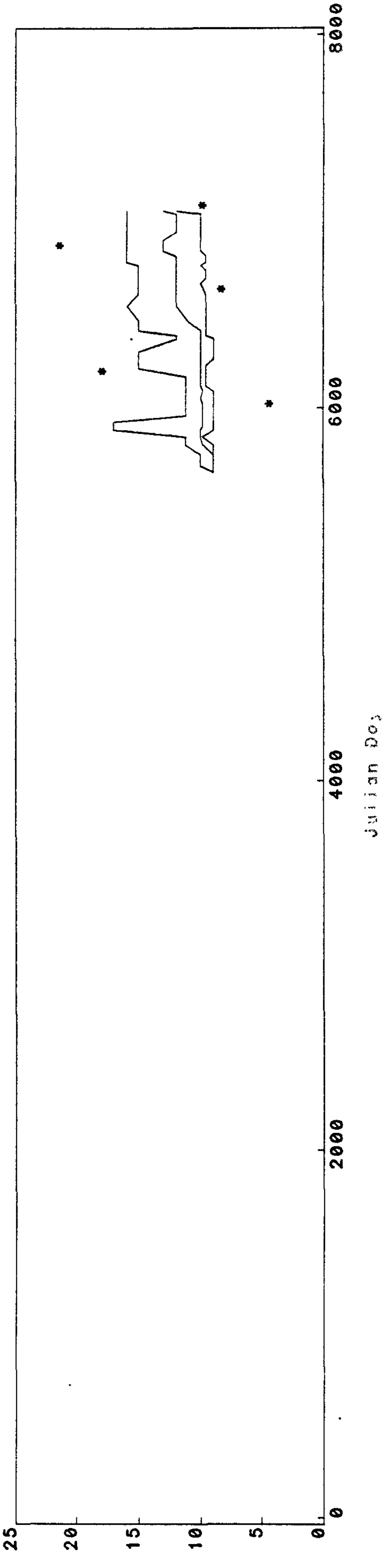
River no 10 DOC

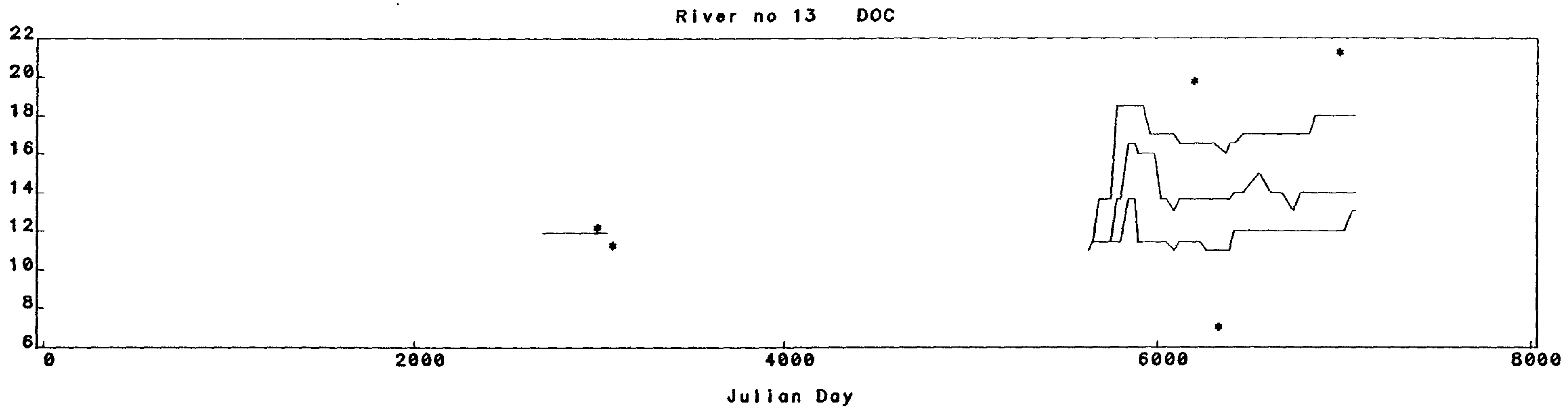


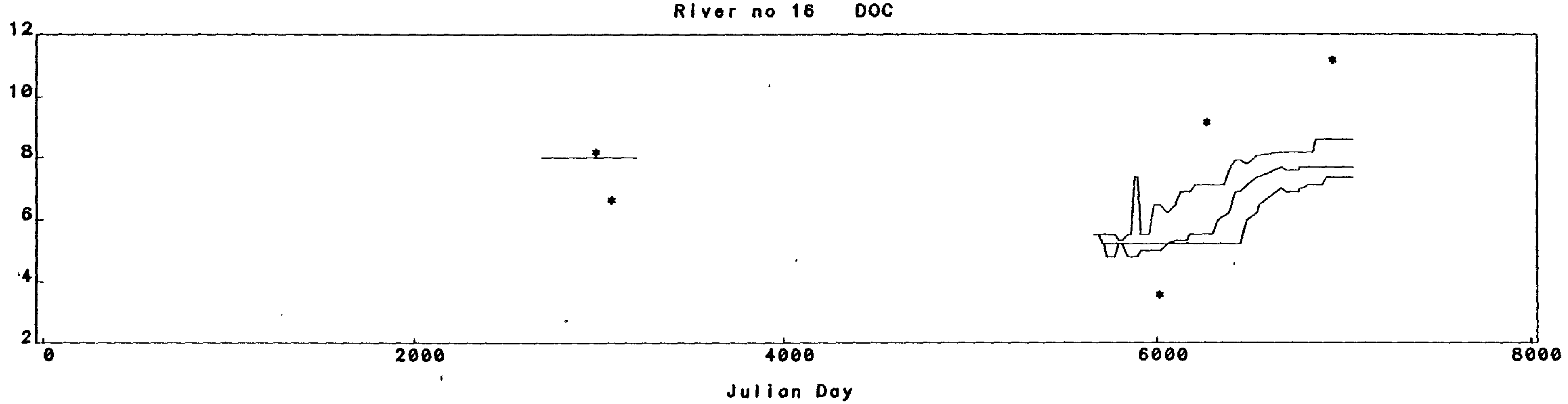
River no 11 DOC

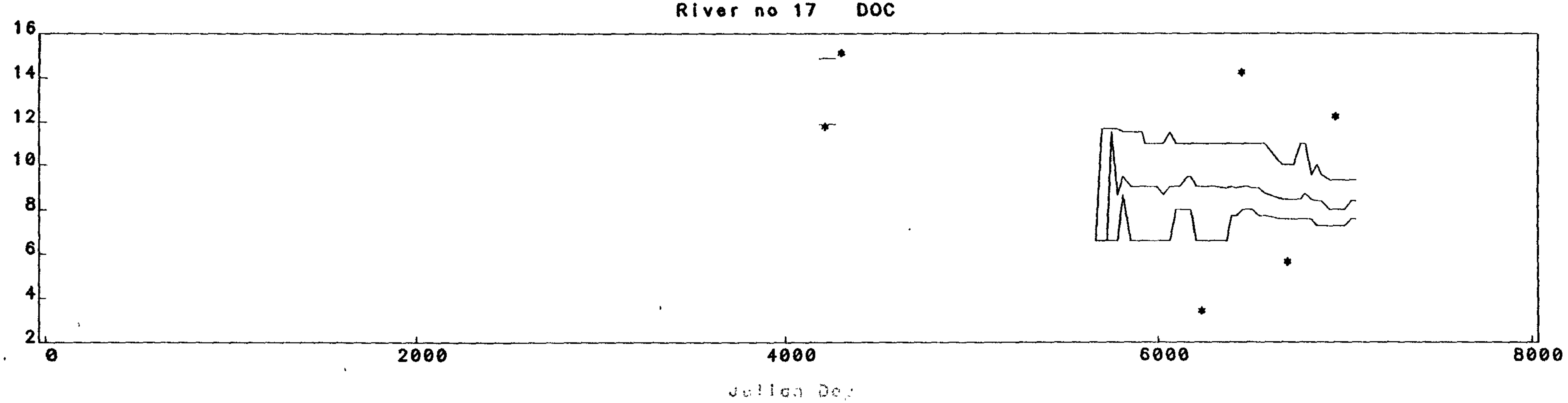


River no 12 DOC




River no 13 DOC
22
20
18
16
14
12
10
8
6
0
2000
4000
6000
8000
Julian Day


River no 16 DOC
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day


River no 17 DOC
16
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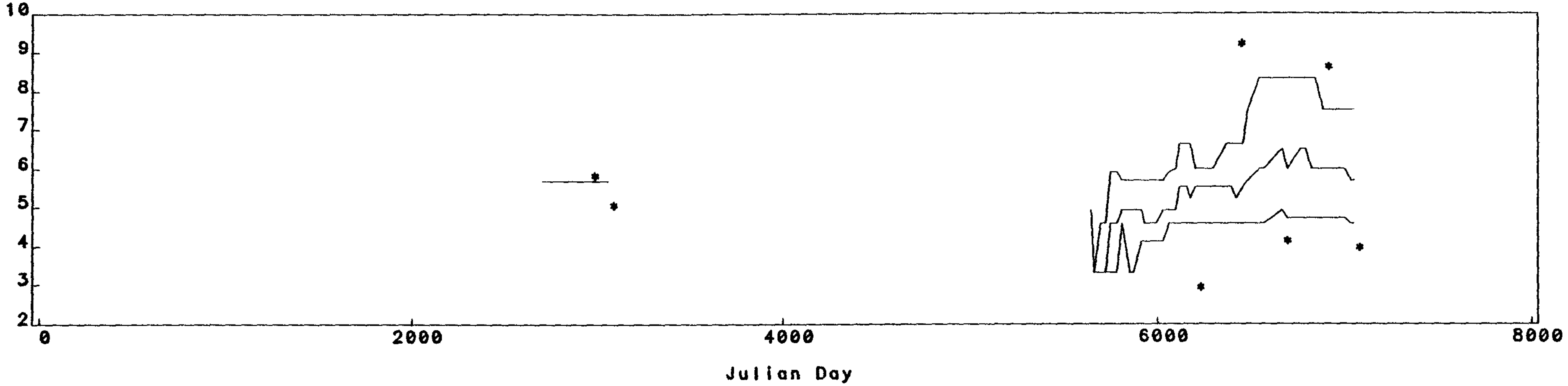
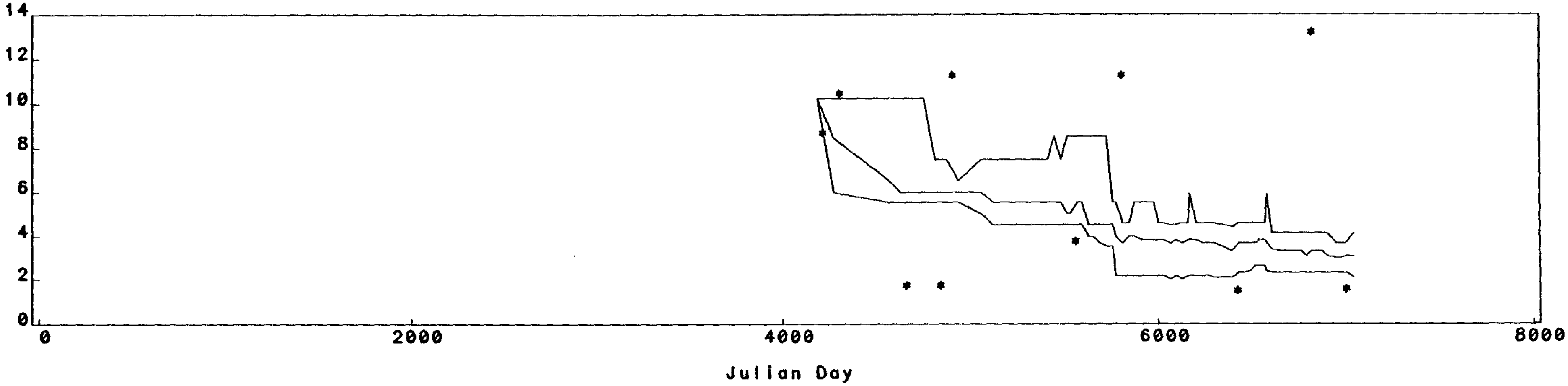
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day

River no 18 DOC



River no 19 DOC



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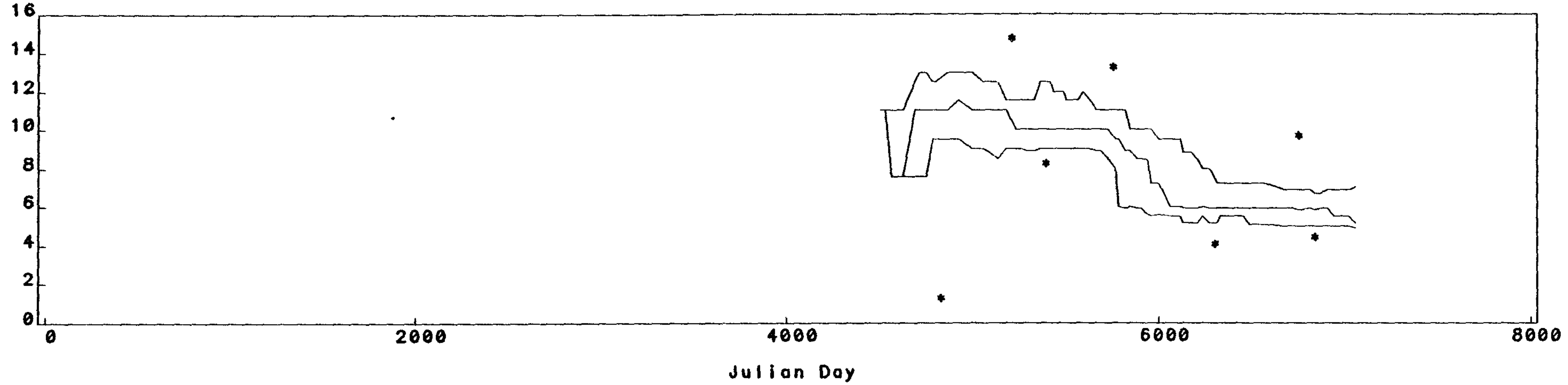

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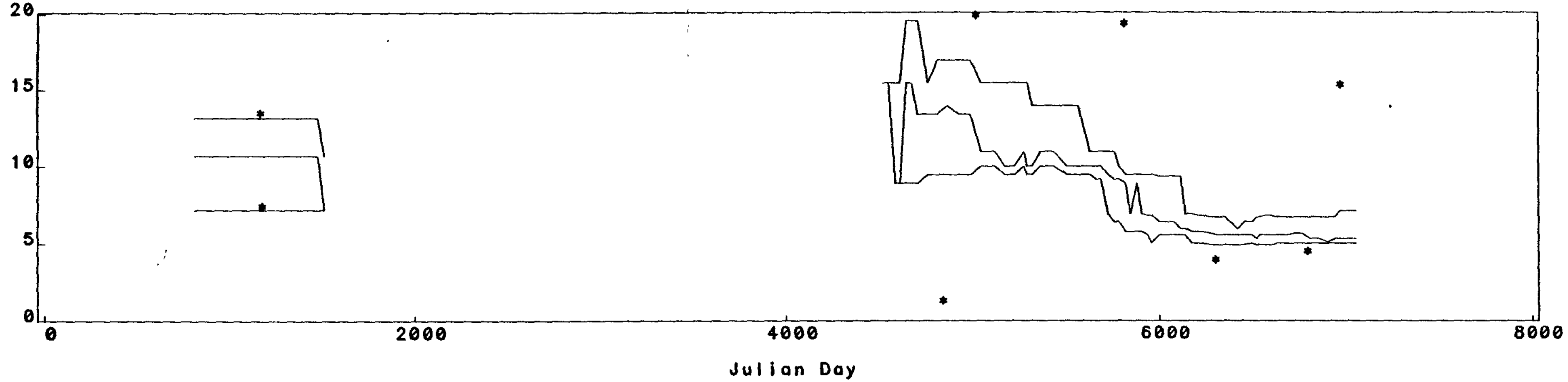

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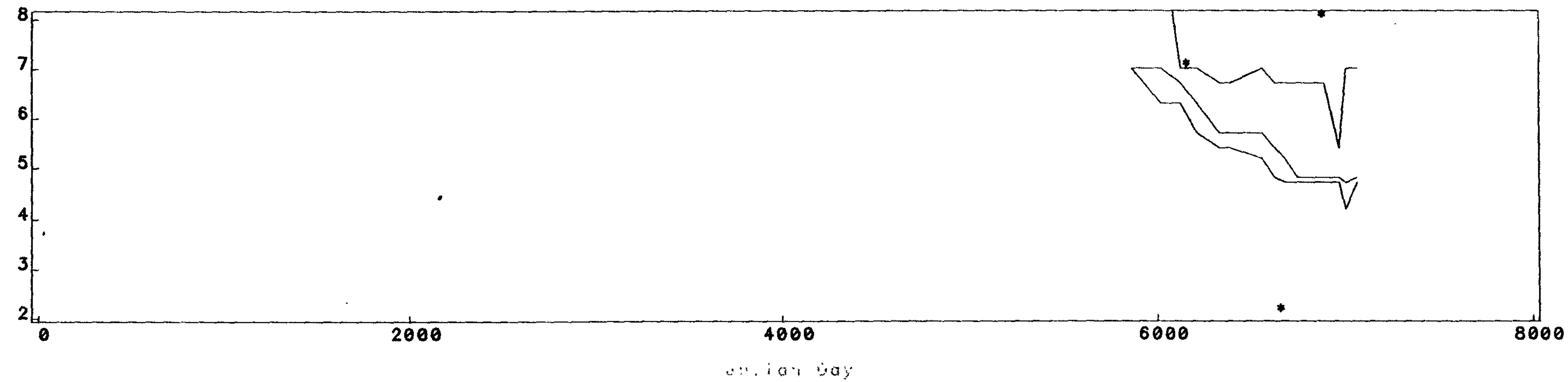
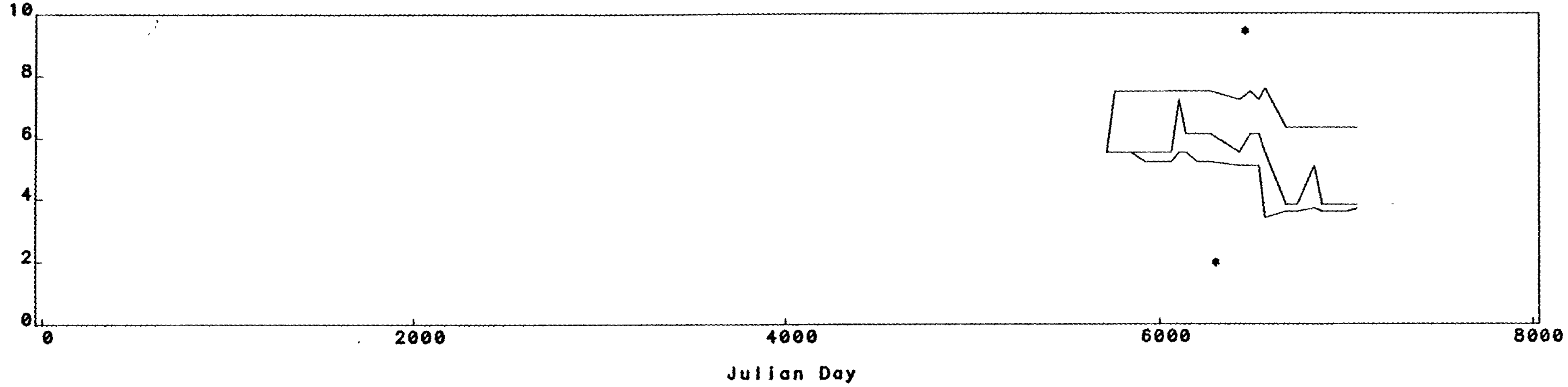
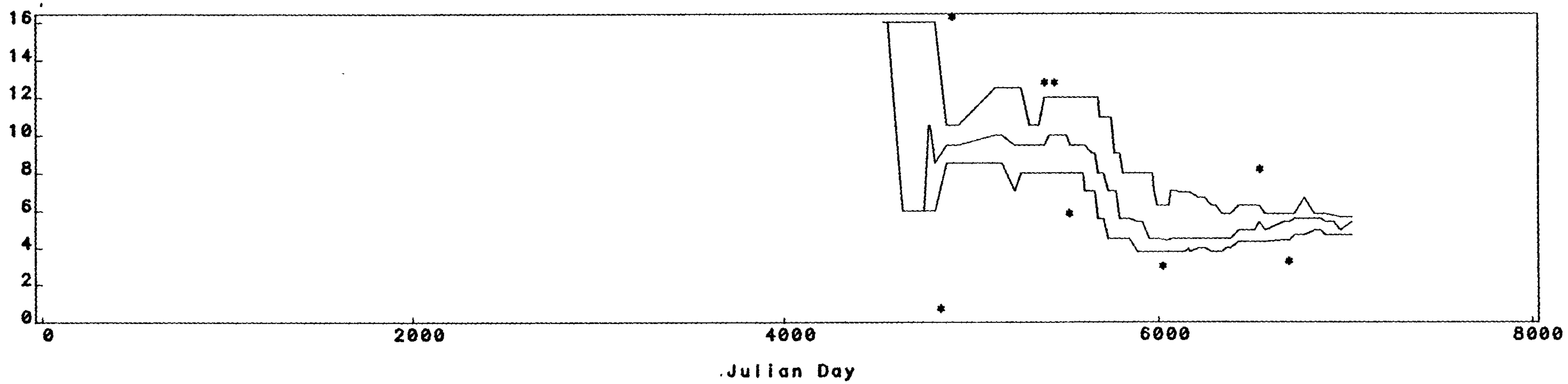


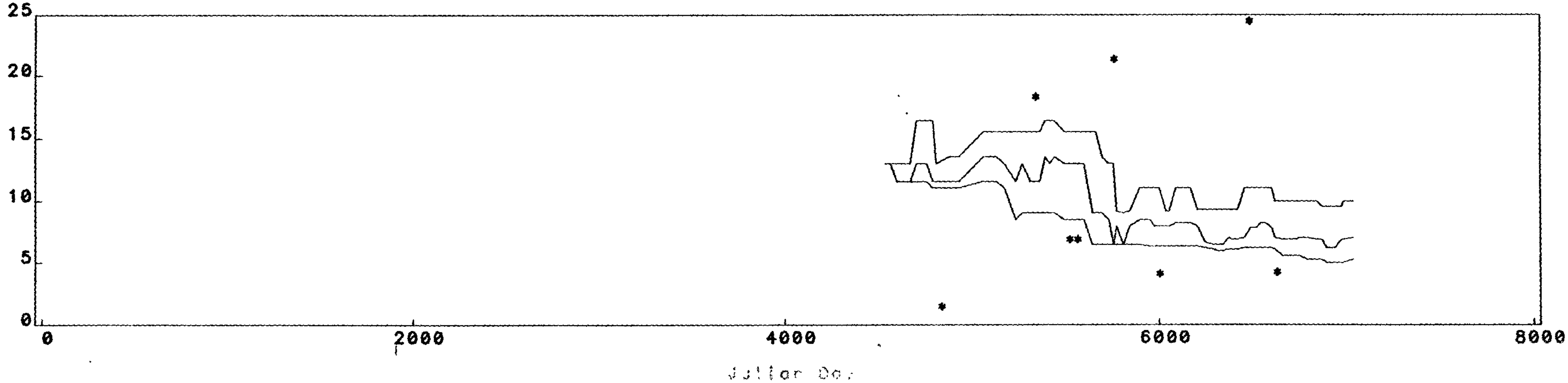
River no 25 DOC

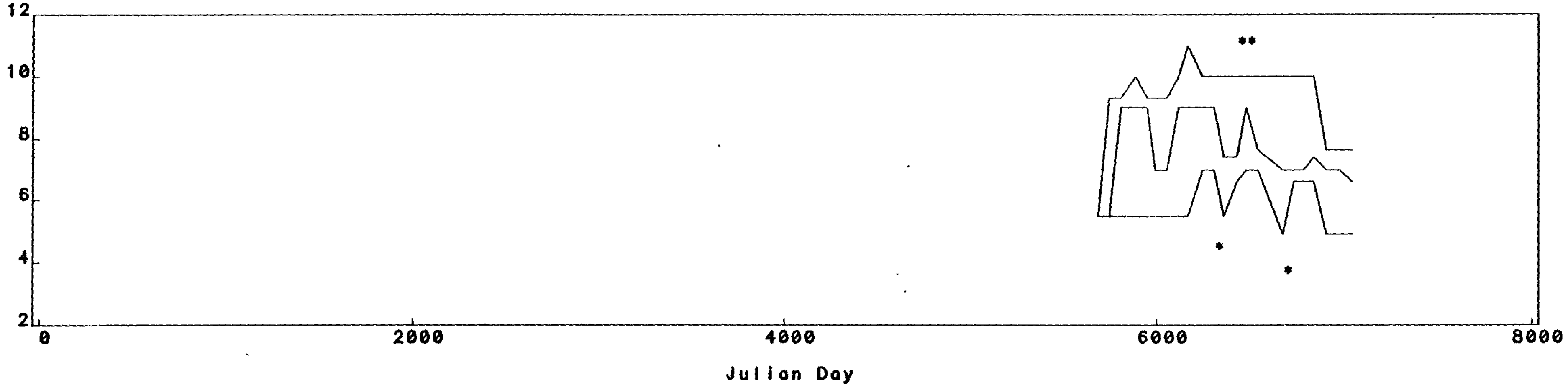


River no 26 DOC



River no 27 DOC

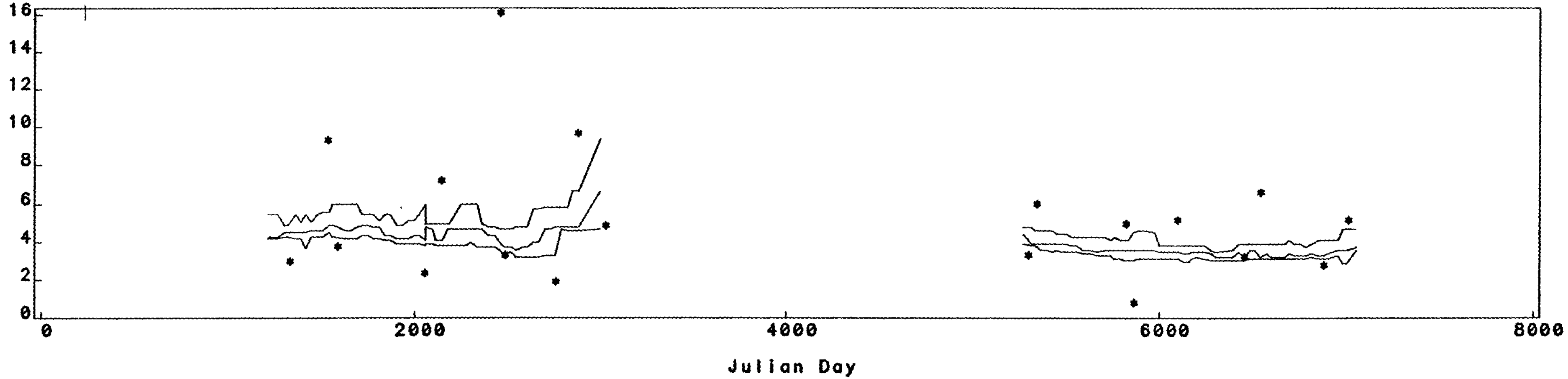




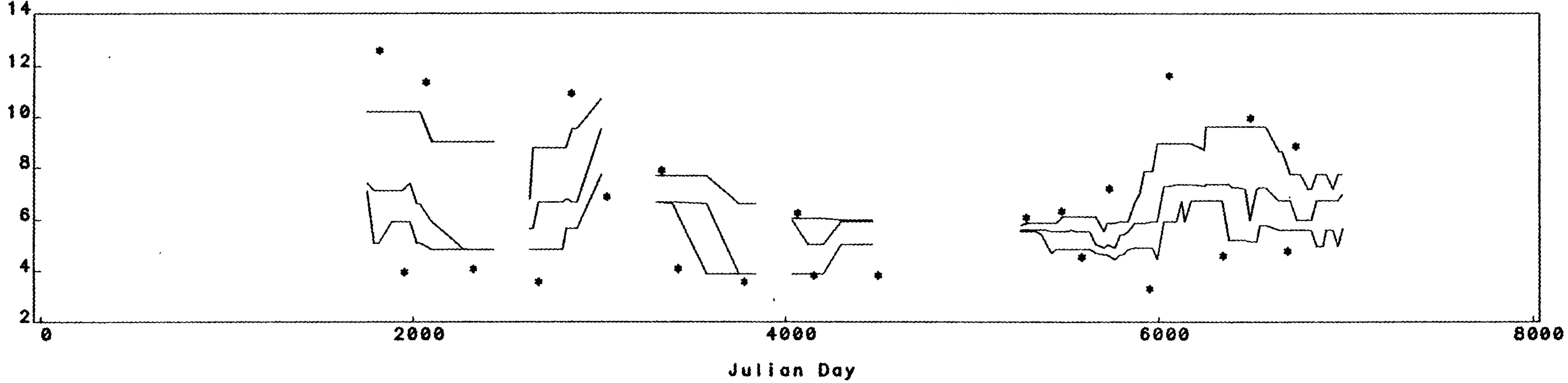
River no 28 DOC

Figure 10. Running boxplots of excess sulfate calculated by chloride ratio for the study rivers.

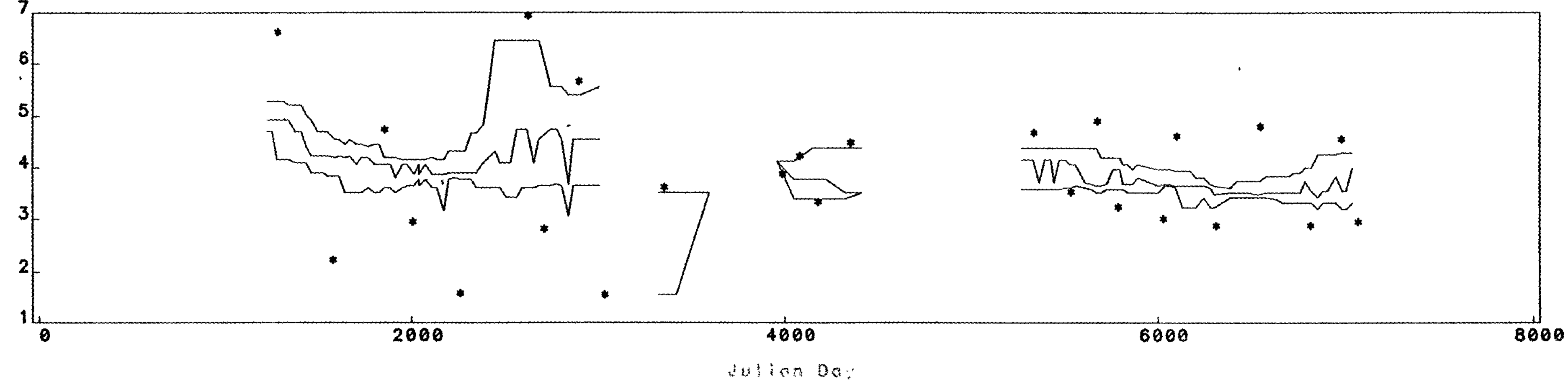
River no 1 Excess SO4 (Cl)



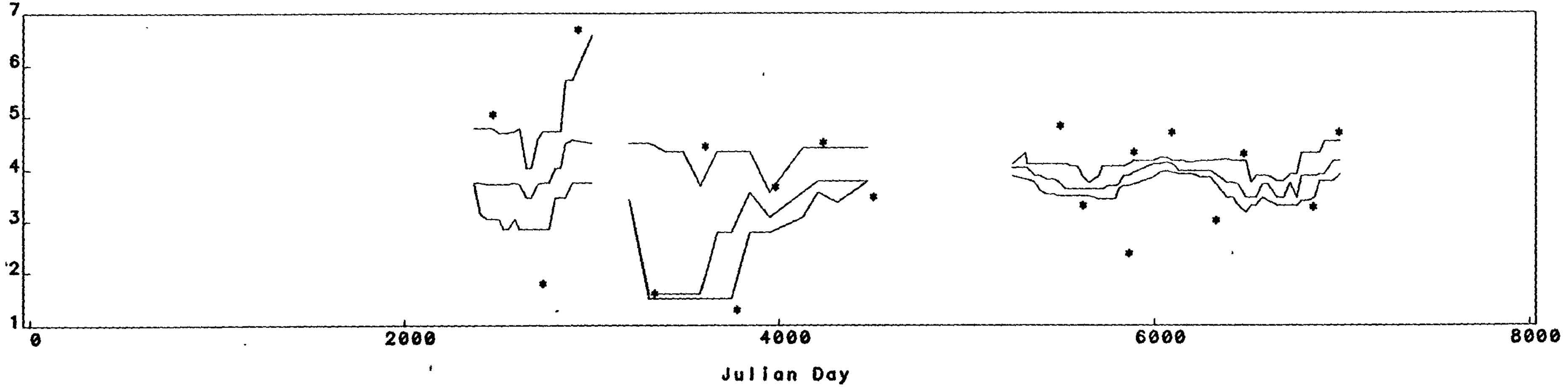
River no 2 Excess SO4 (Cl)



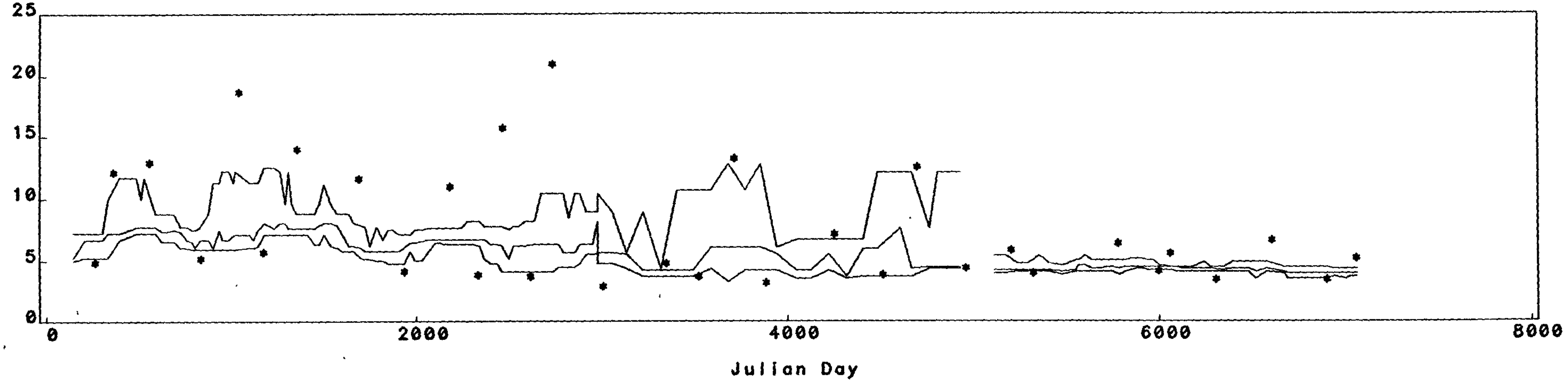
River no 3 Excess SO4 (Cl)



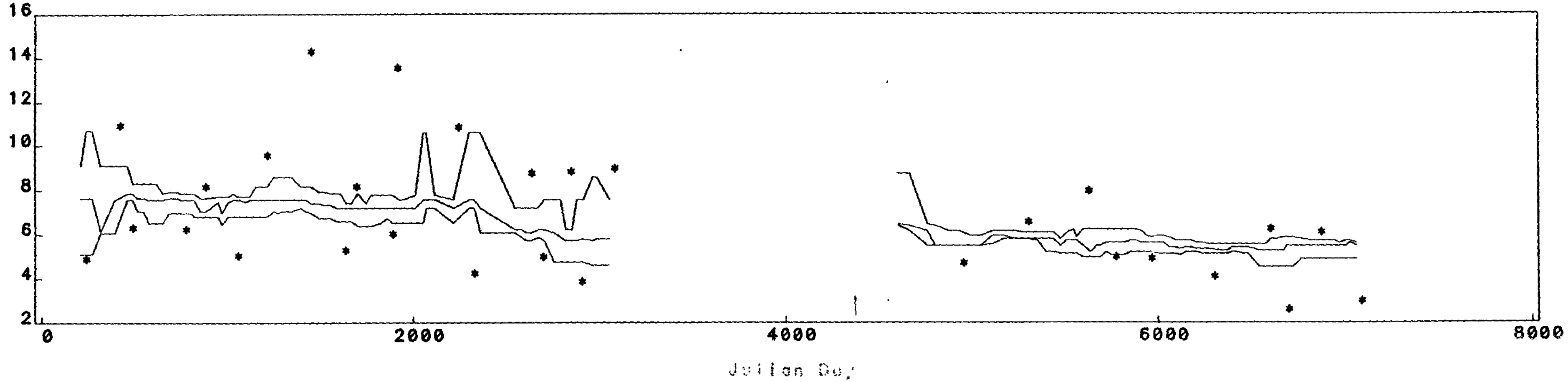
River no 4 Excess SO4 (Cl)



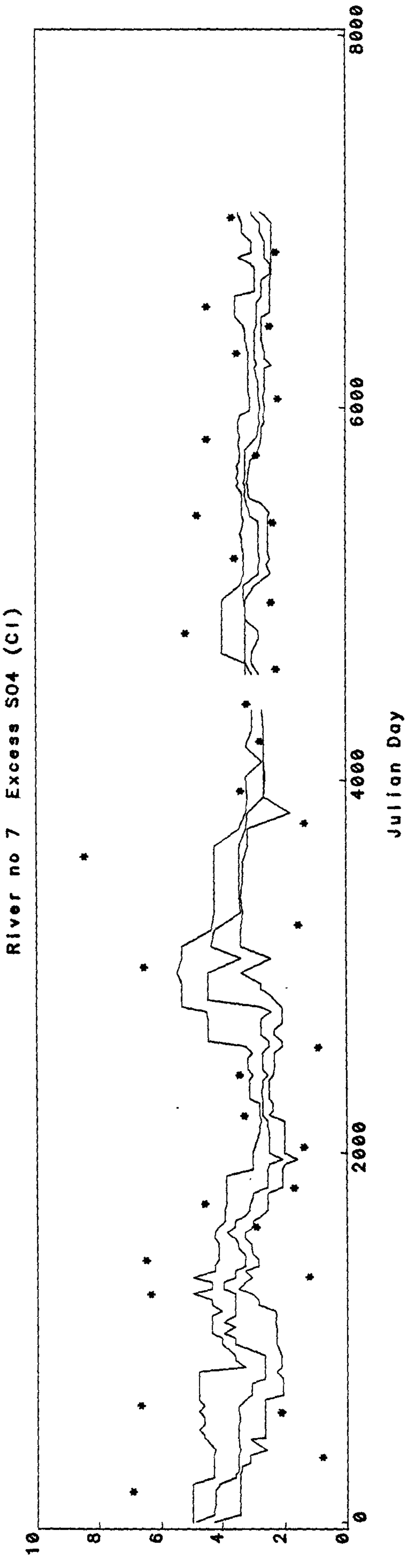
River no 5 Excess SO4 (Cl)



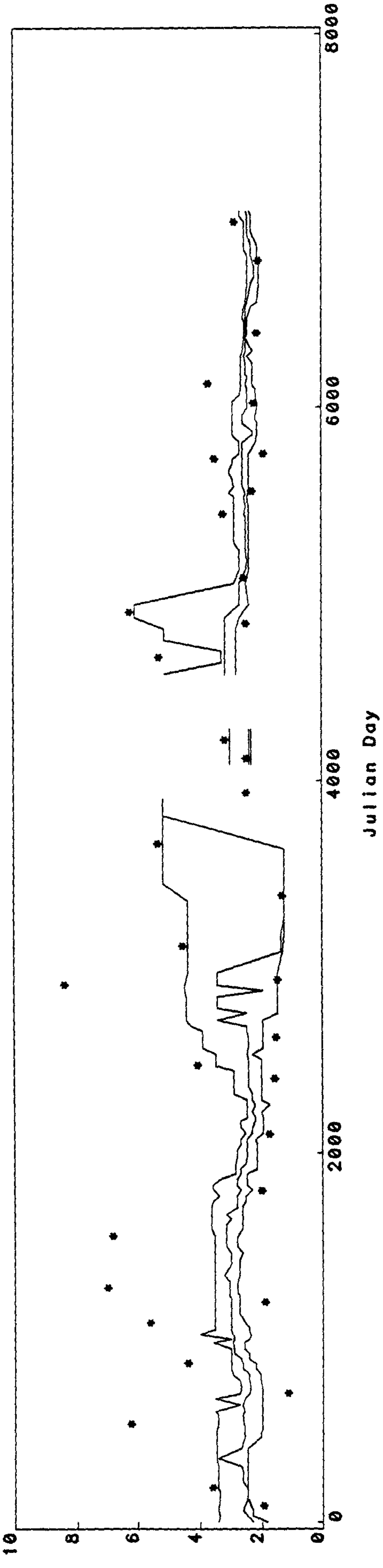
River no 6 Excess SO4 (Cl)



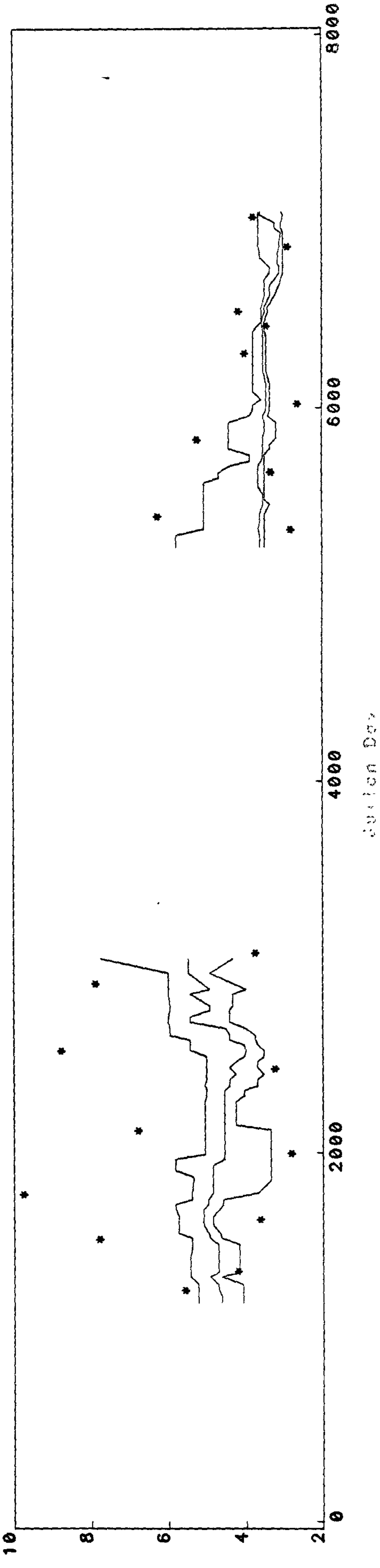
River no 7 Excess SO4 (Cl)

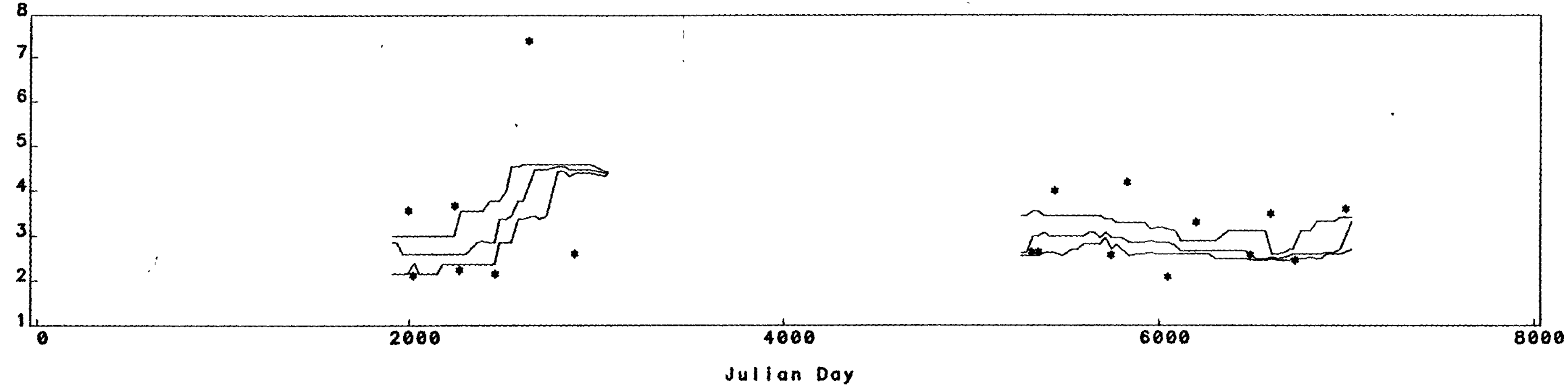


River no 8 Excess SO4 (Cl)

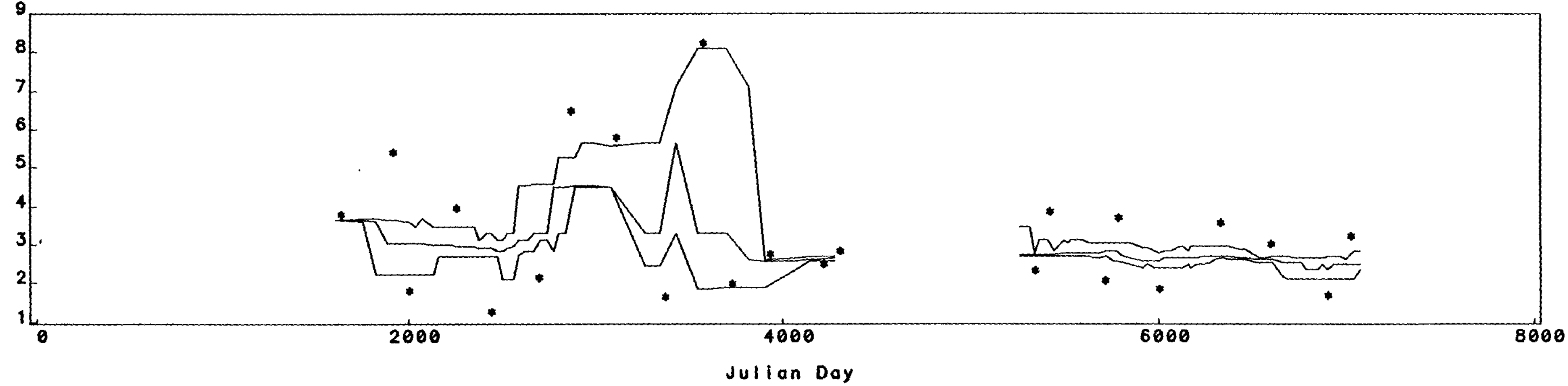


River no 9 Excess SO4 (Cl)





River no 10 Excess SO4 (Cl)



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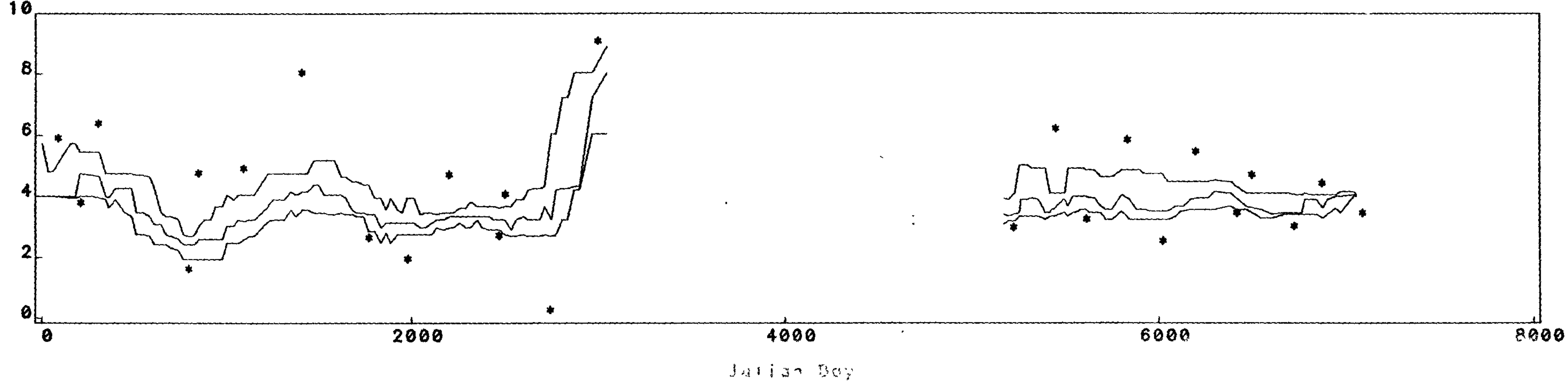
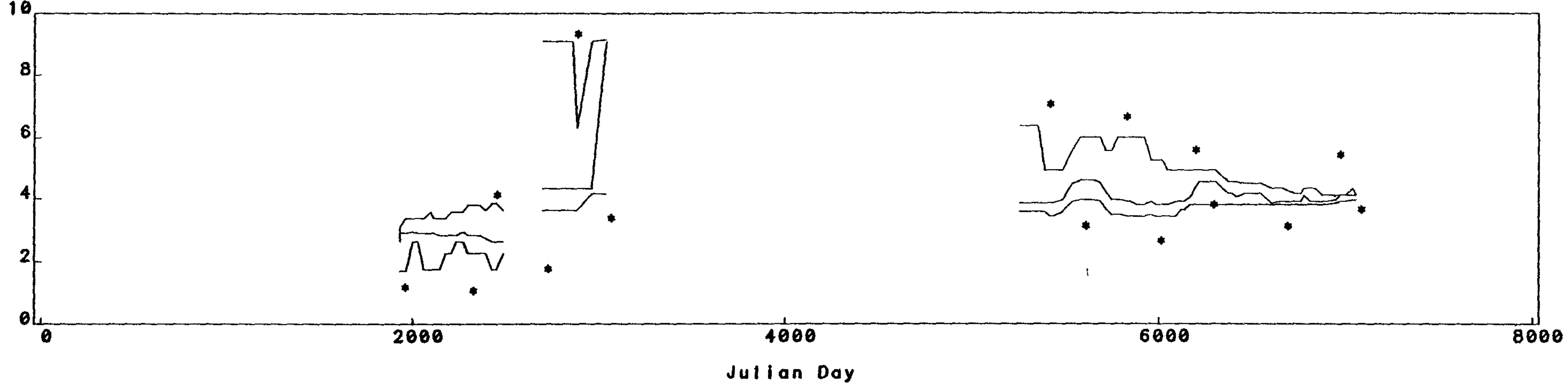
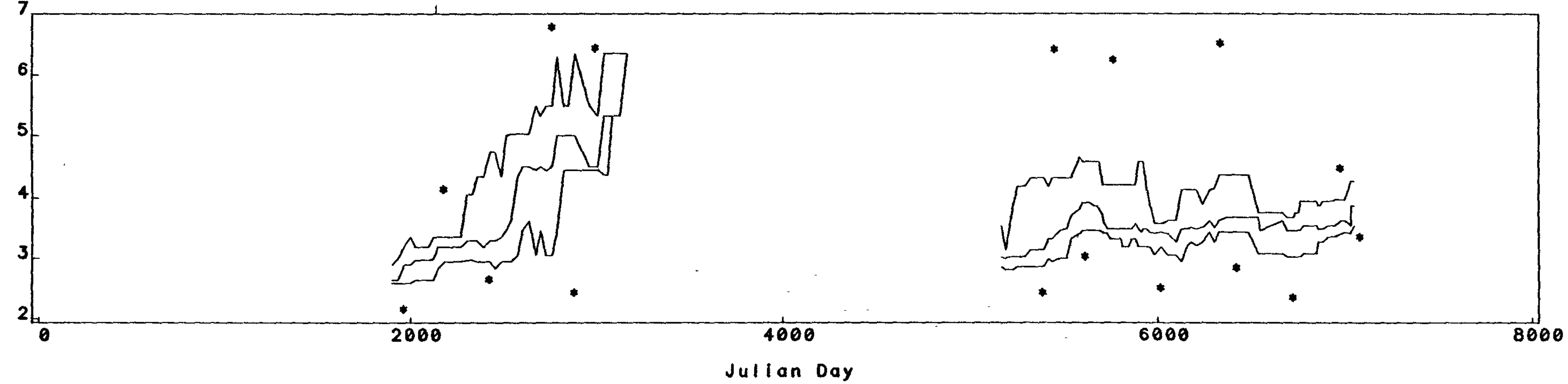


River no 12 Excess SO4 (Cl)

River no 13 Excess SO4 (Cl)



River no 16 Excess SO4 (Cl)



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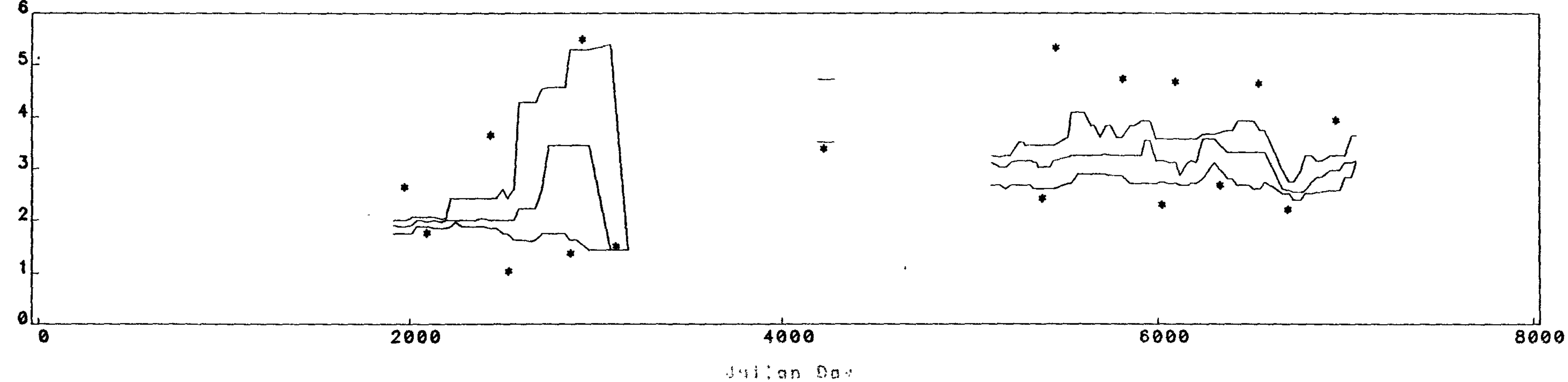
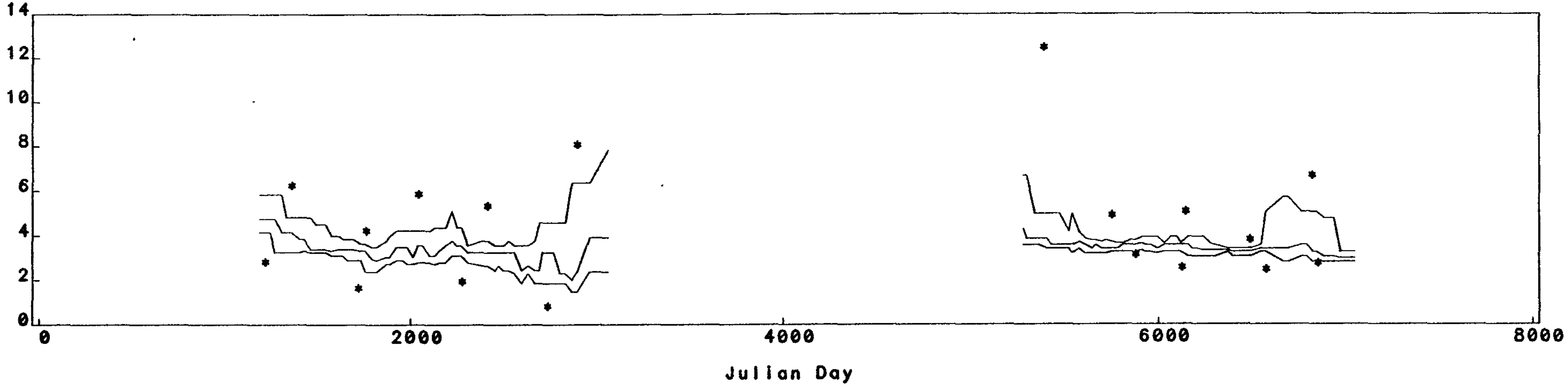
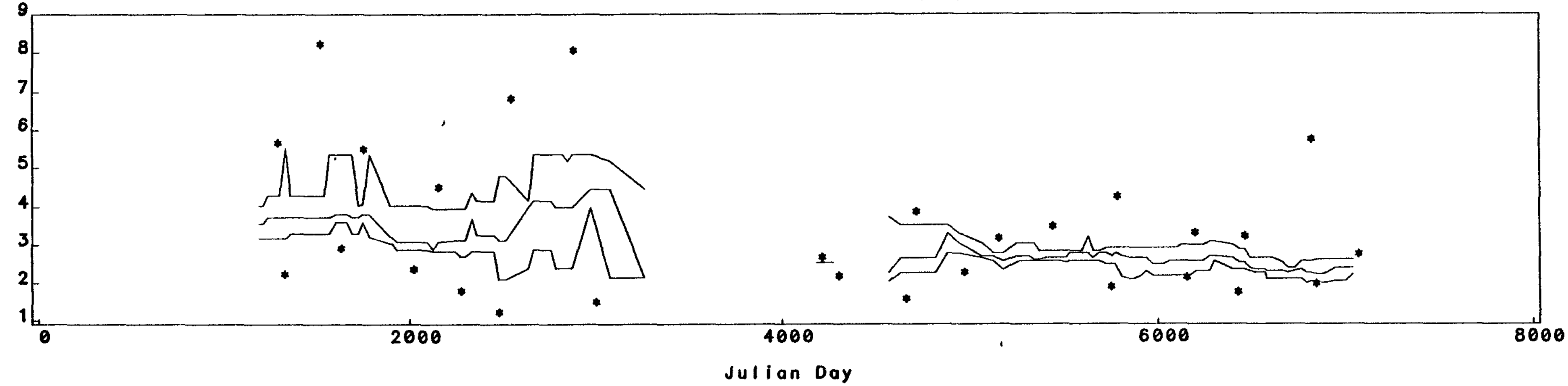


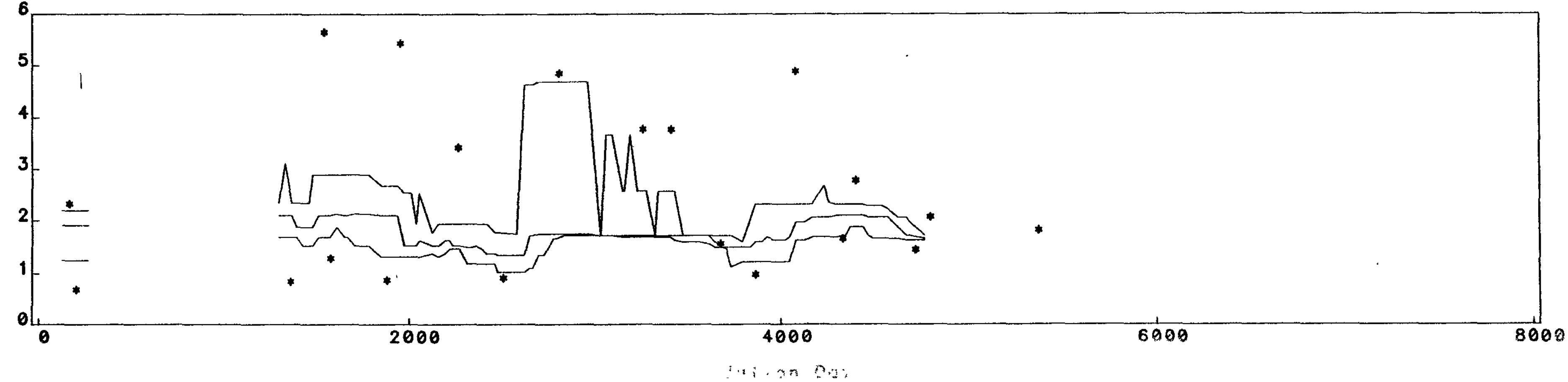
River no 18 Excess SO4 (Cl)



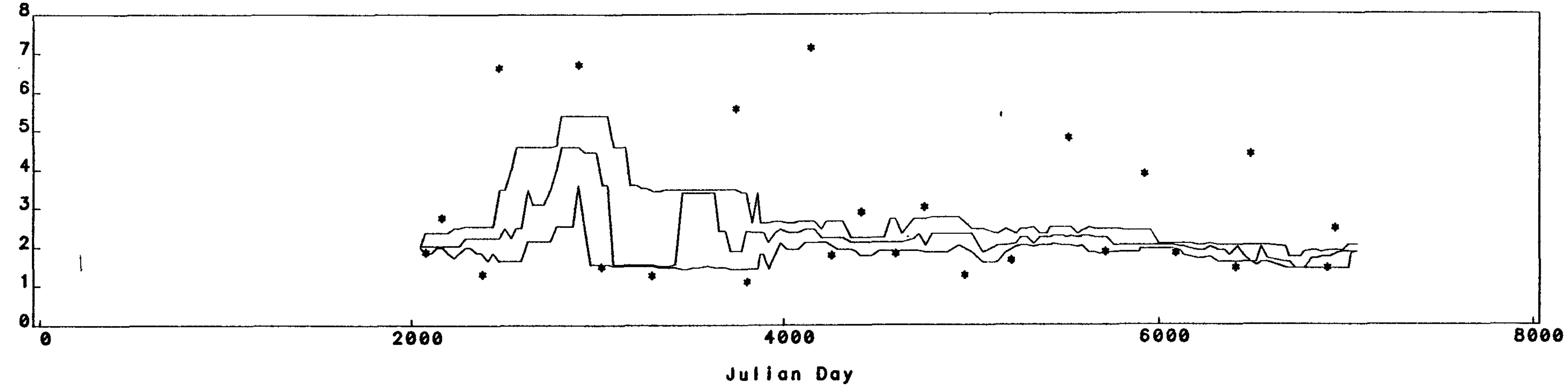
River no 19 Excess SO4 (Cl)



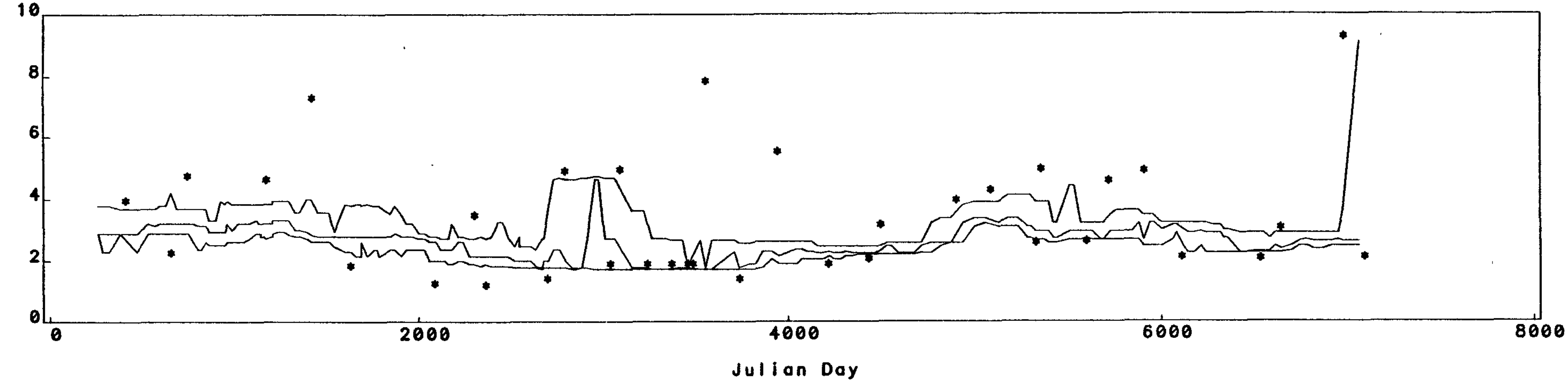
River no 20 Excess SO4 (Cl)



River no 21 Excess SO4 (Cl)



River no 22 Excess SO4 (Cl)



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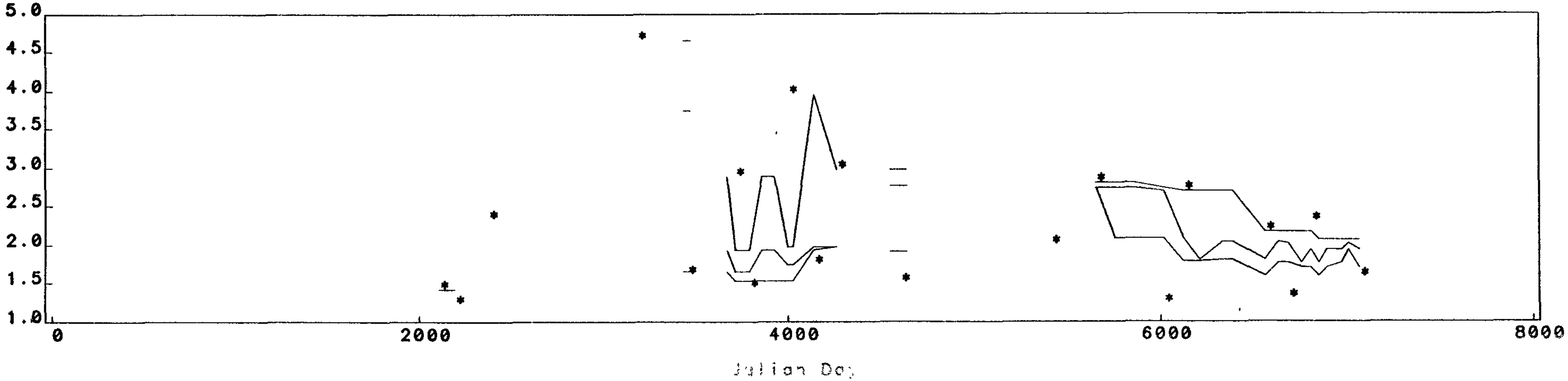
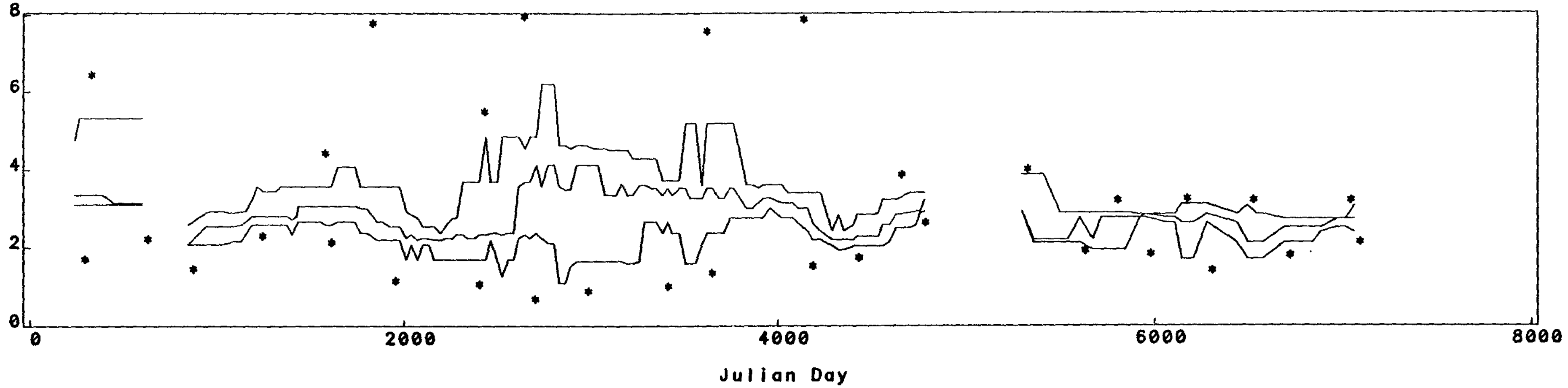


River no 25 Excess SO4 (Cl)



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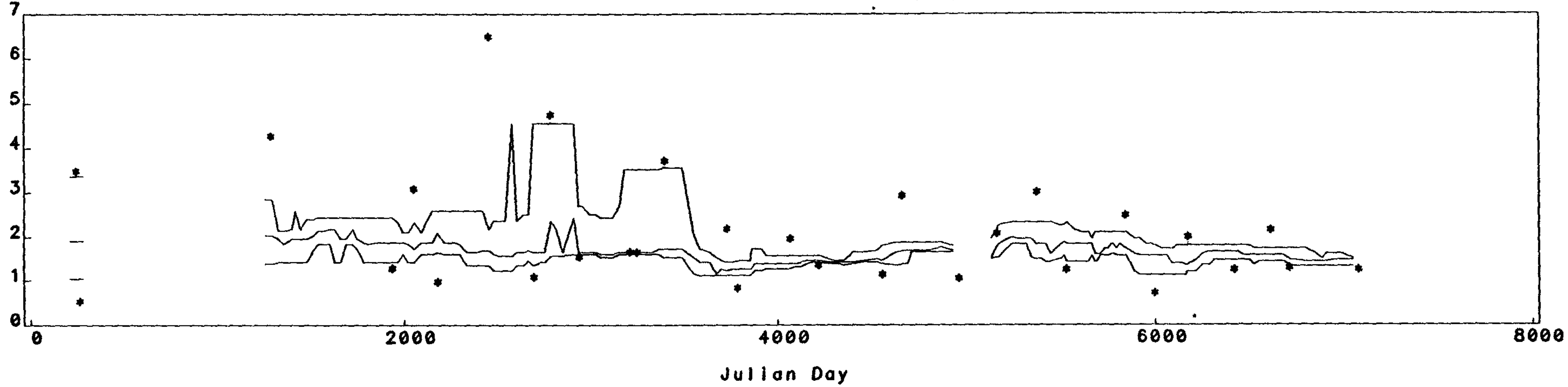
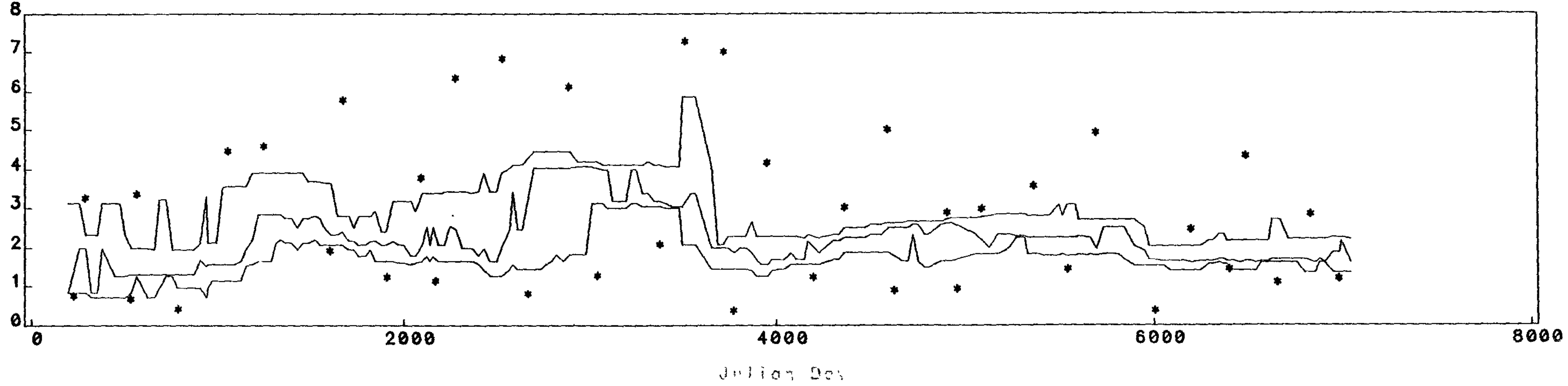
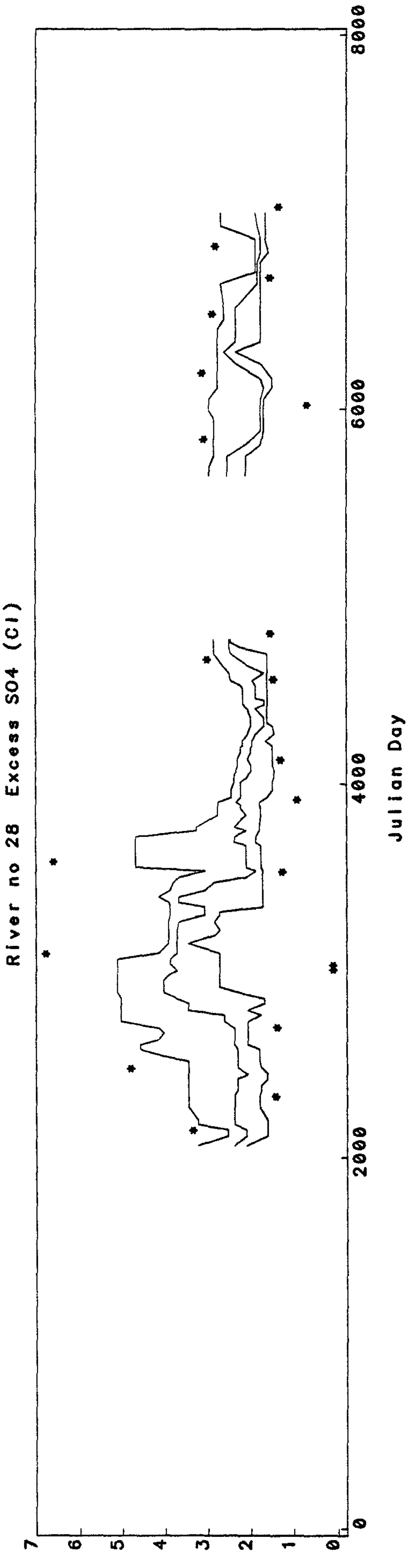
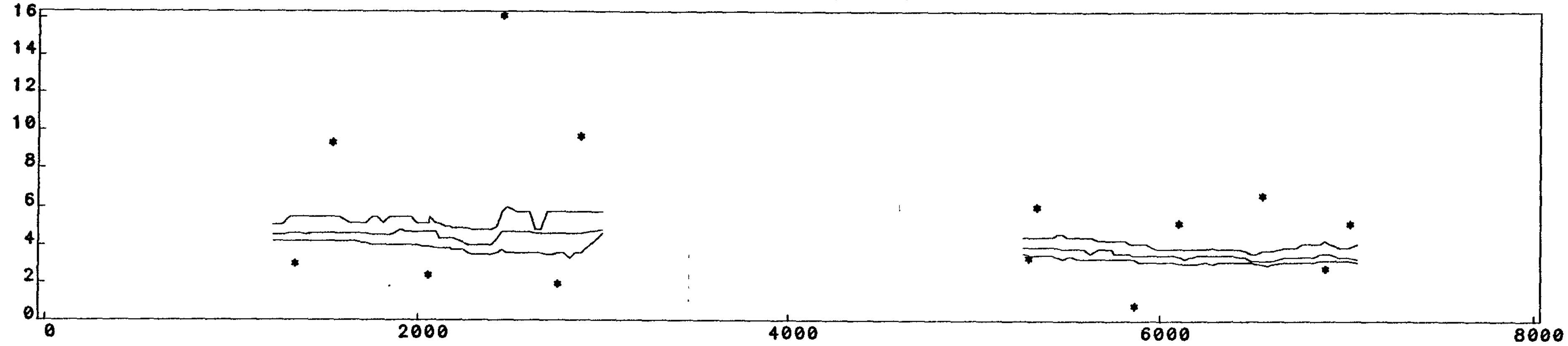


River no 27 Excess SO4 (Cl)

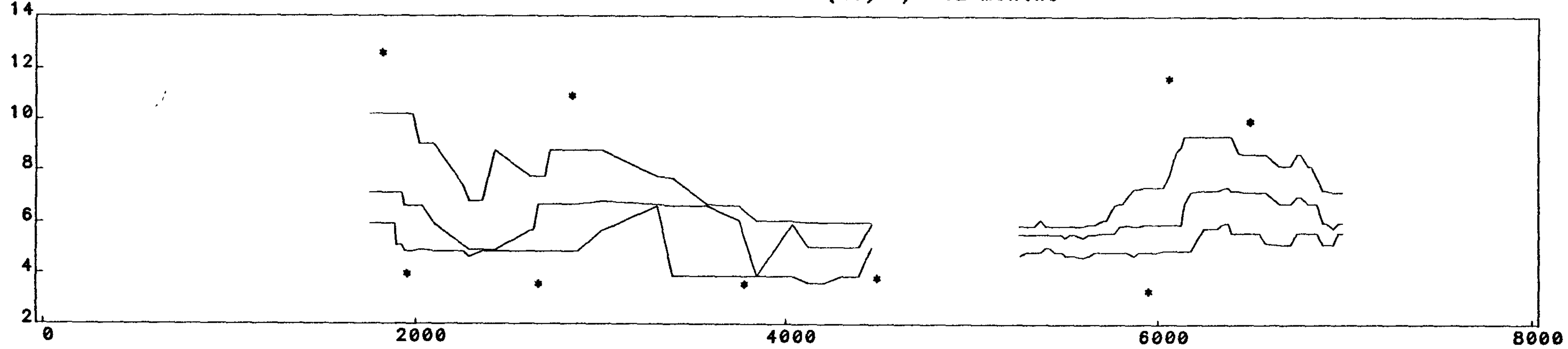



River no 28 Excess SO4 (Cl)

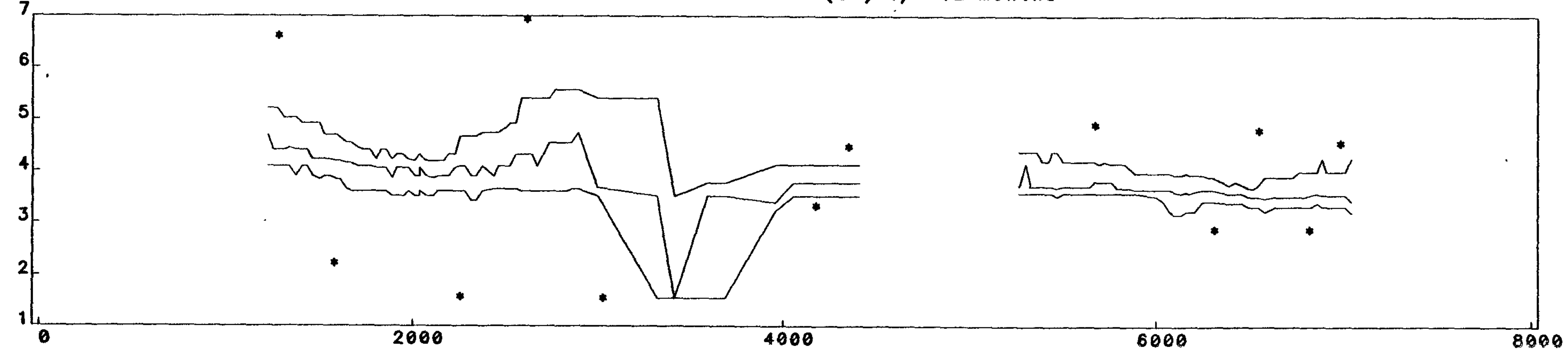
River no 1 Excess SO4 (Cl) +/- 12 months

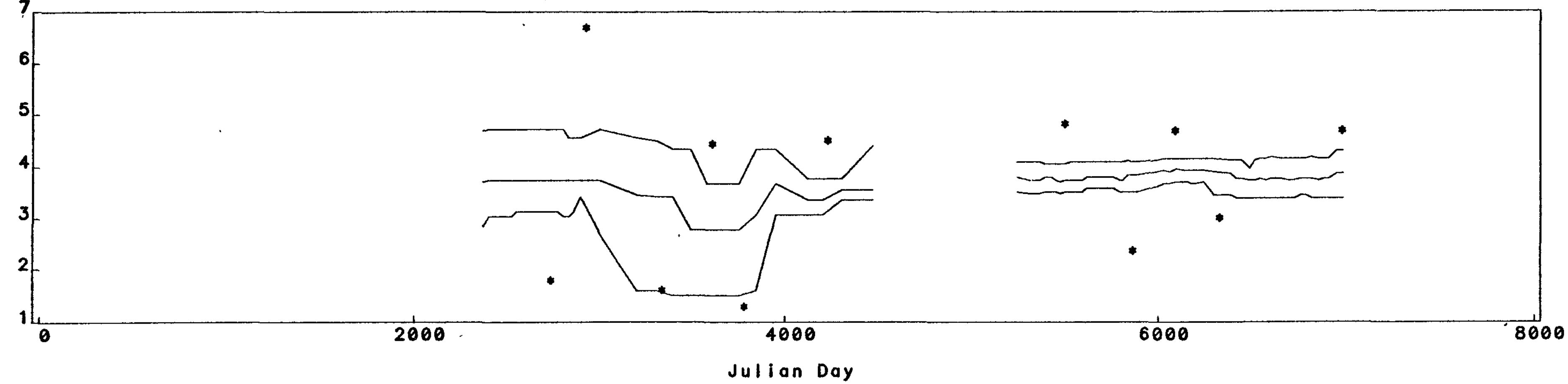


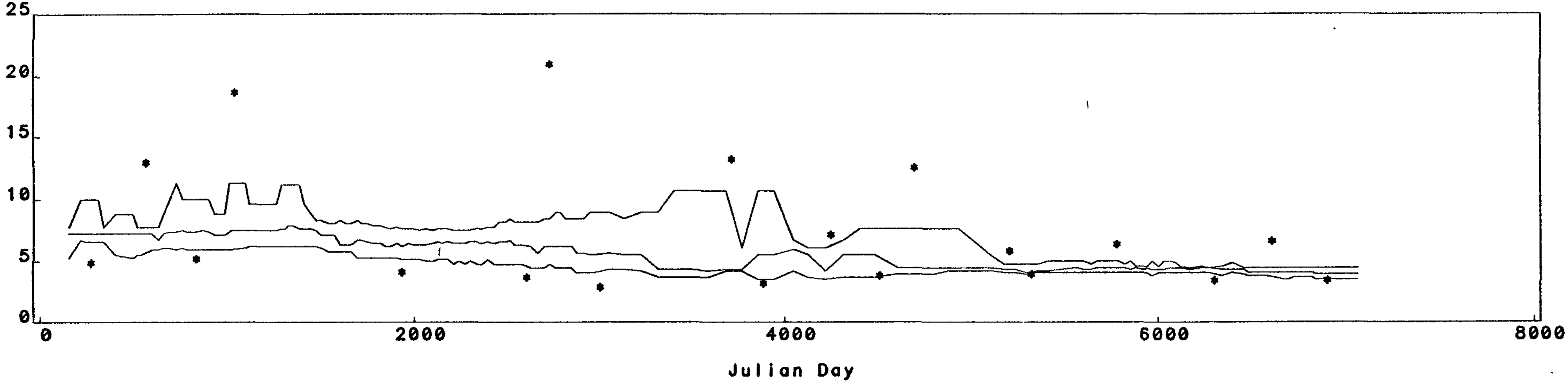
River no 2 Excess SO4 (Cl) +/- 12 months

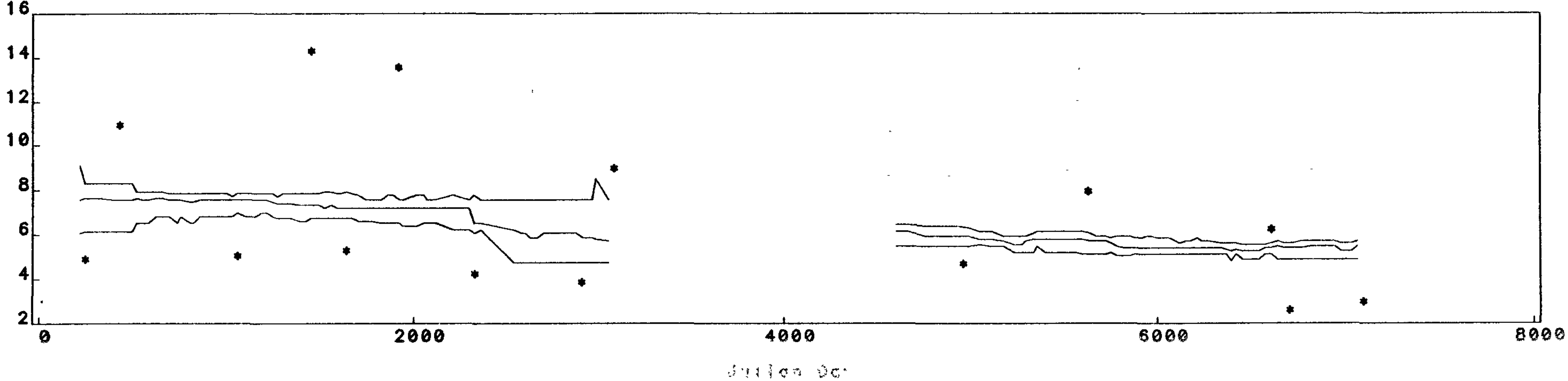


River no 3 Excess SO4 (Cl) +/- 12 months

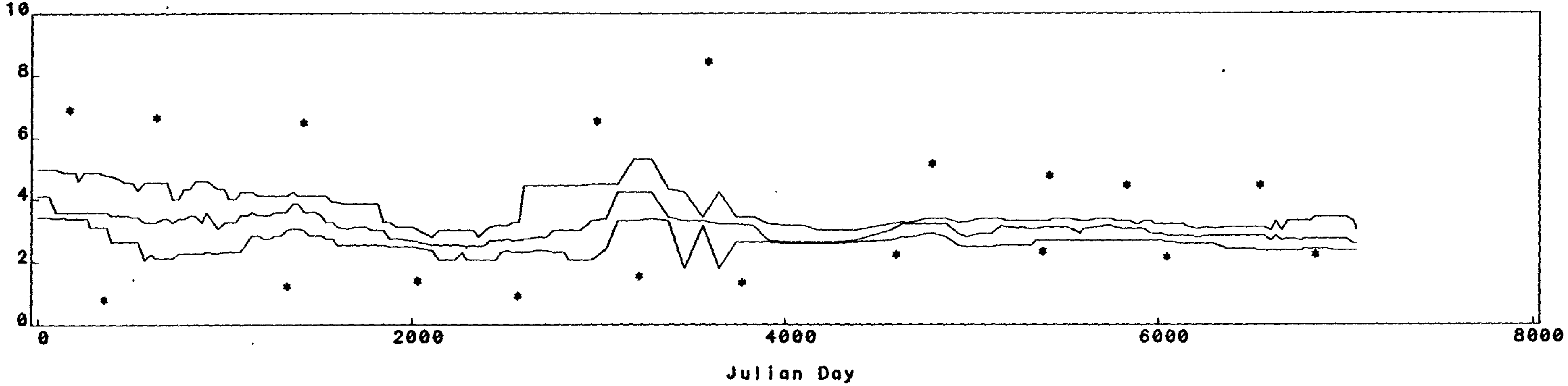



River no 4 Excess SO4 (Cl) +/- 12 months

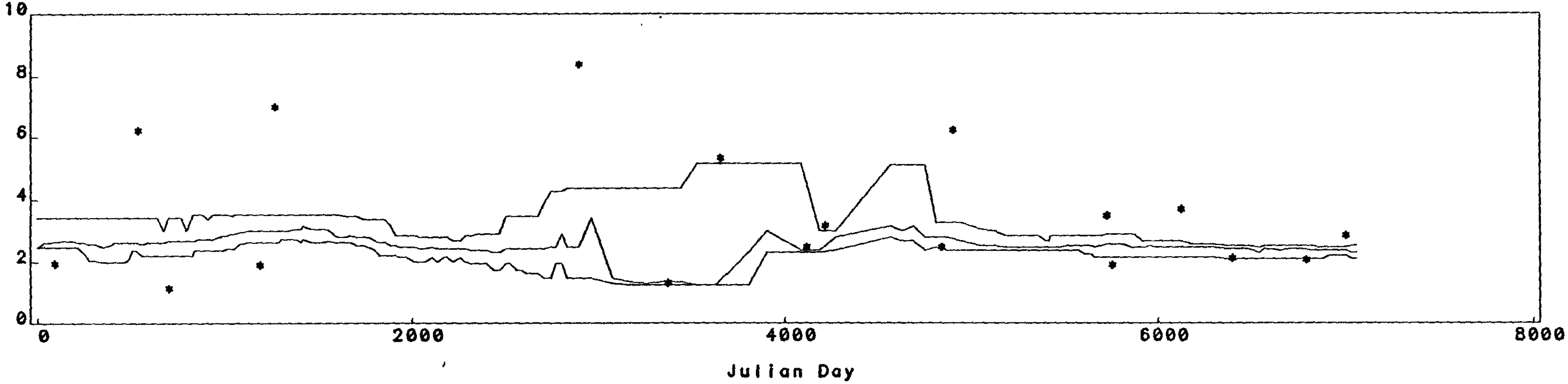

River no 5 Excess SO4 (Cl) +/- 12 months


River no 6 Excess SO4 (Cl) +/- 12 months

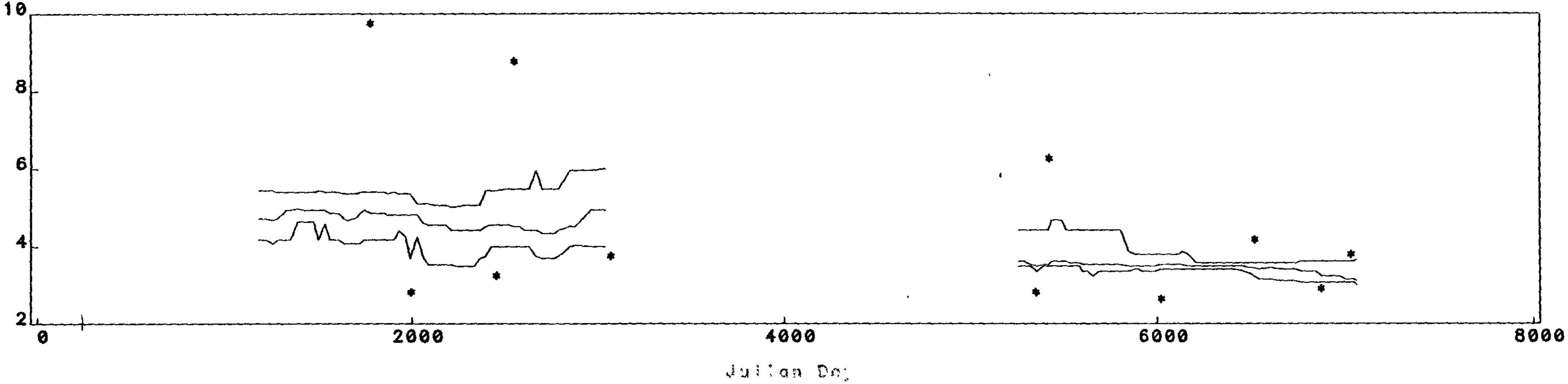
River no 7 Excess SO4 (Cl) +/- 12 months

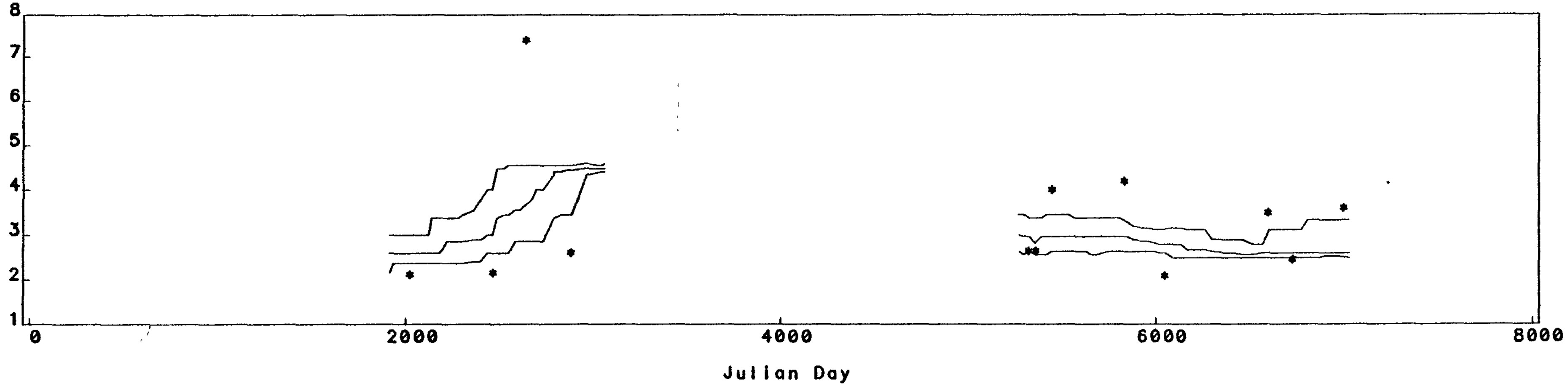


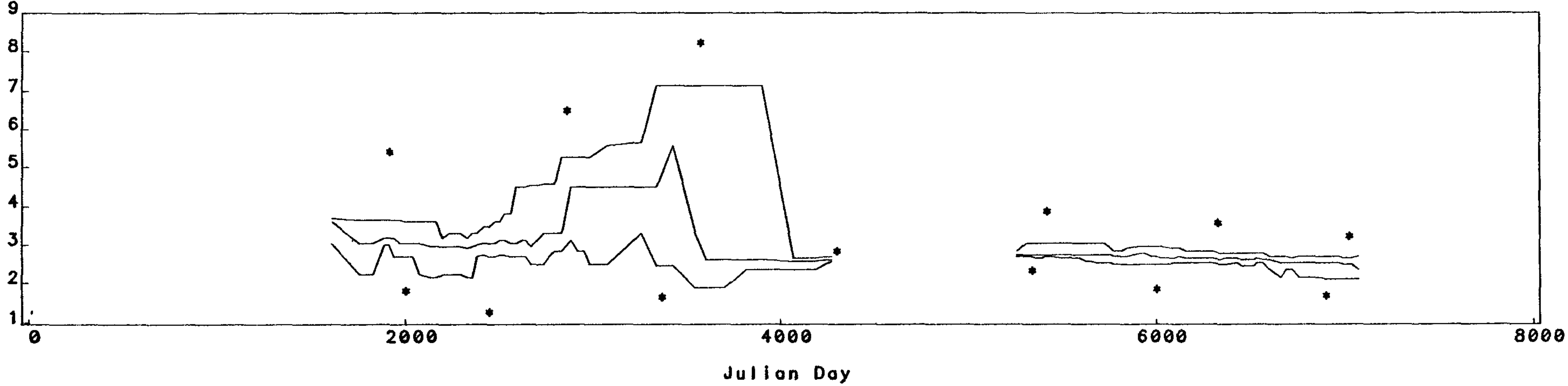
River no 8 Excess SO4 (Cl) +/- 12 months

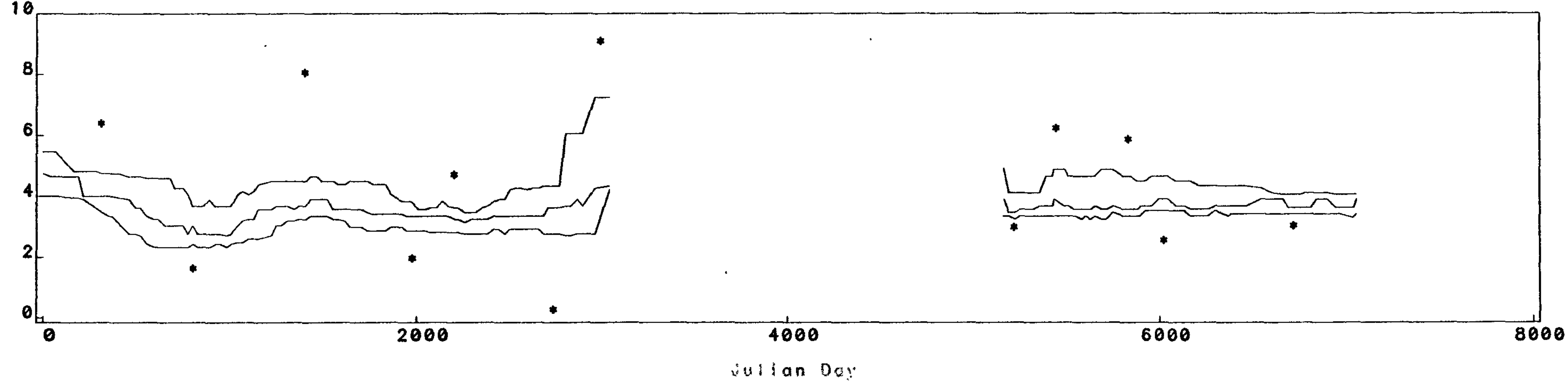


River no 9 Excess SO4 (Cl) +/- 12 months

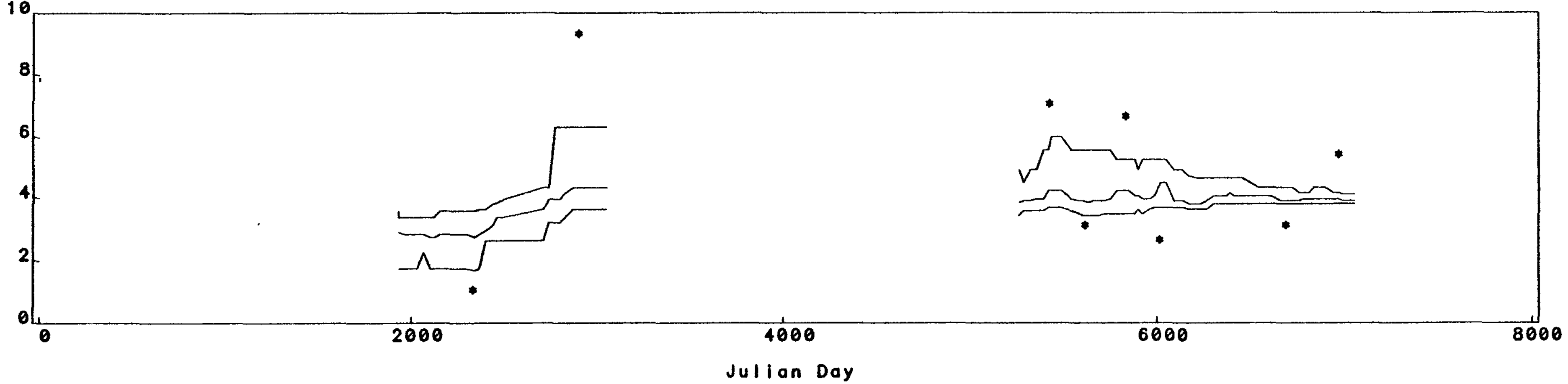



River no 10 Excess SO4 (Cl) +/- 12 months

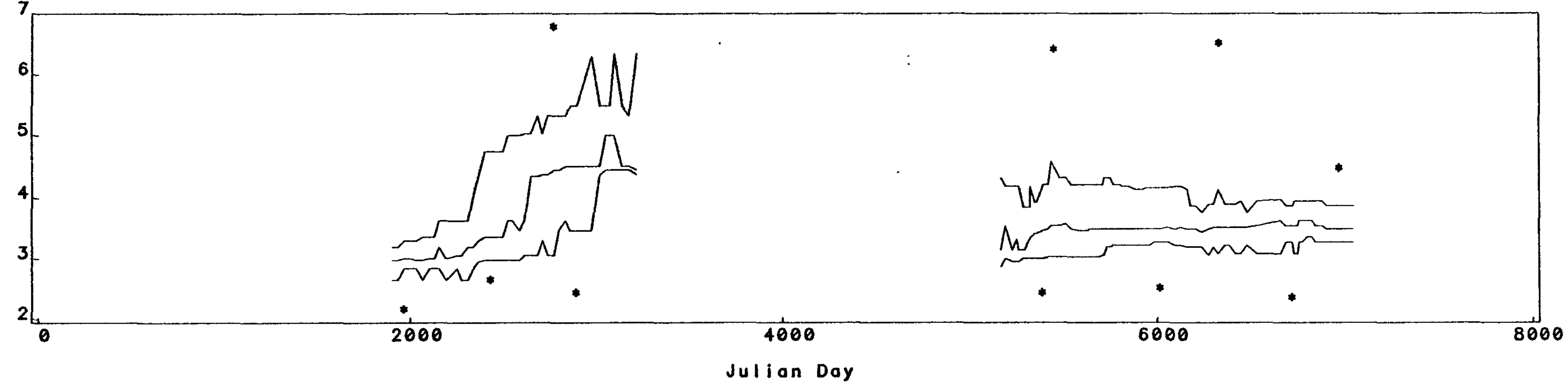

River no 11 Excess SO4 (Cl) +/- 12 months


River no 12 Excess SO4 (Cl) +/- 12 months

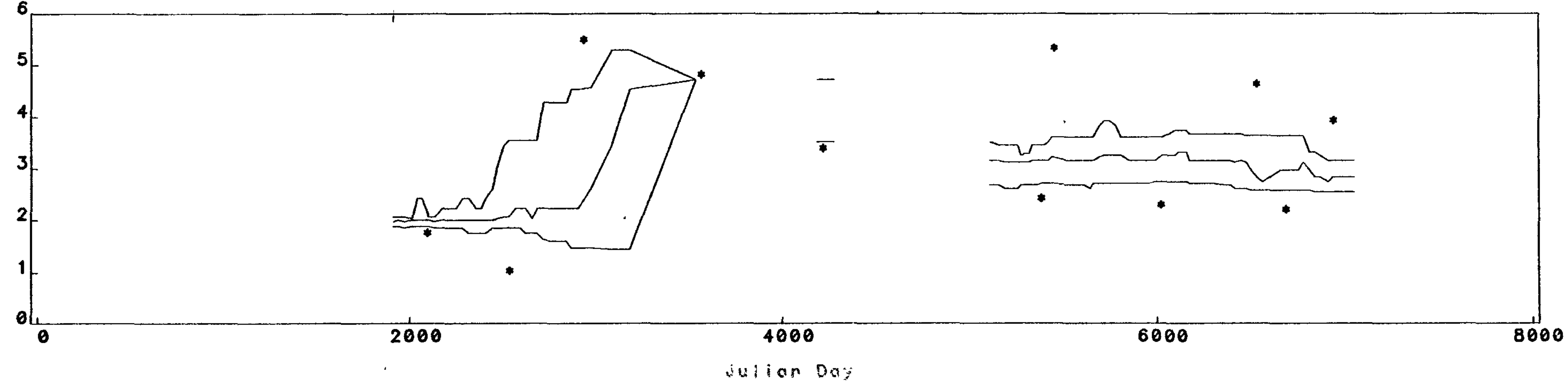
River no 13 Excess SO4 (Cl) +/- 12 months



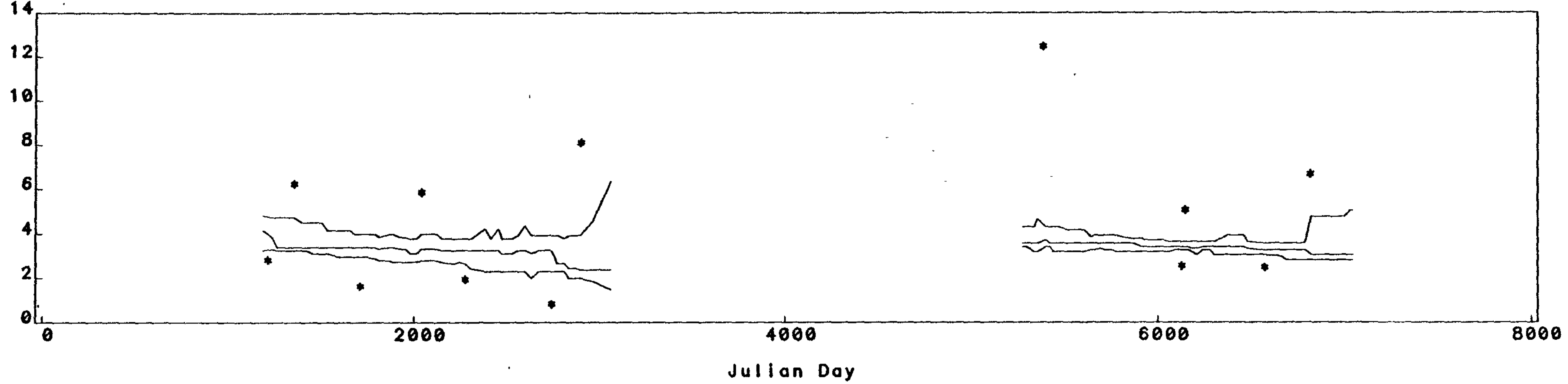
River no 16 Excess SO4 (Cl) +/- 12 months



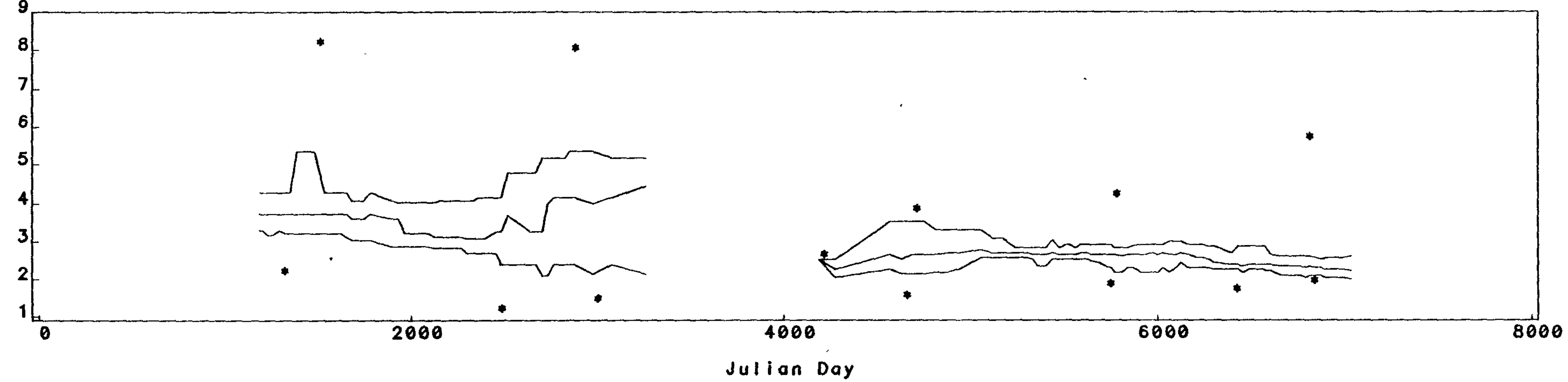
River no 17 Excess SO4 (Cl) +/- 12 months



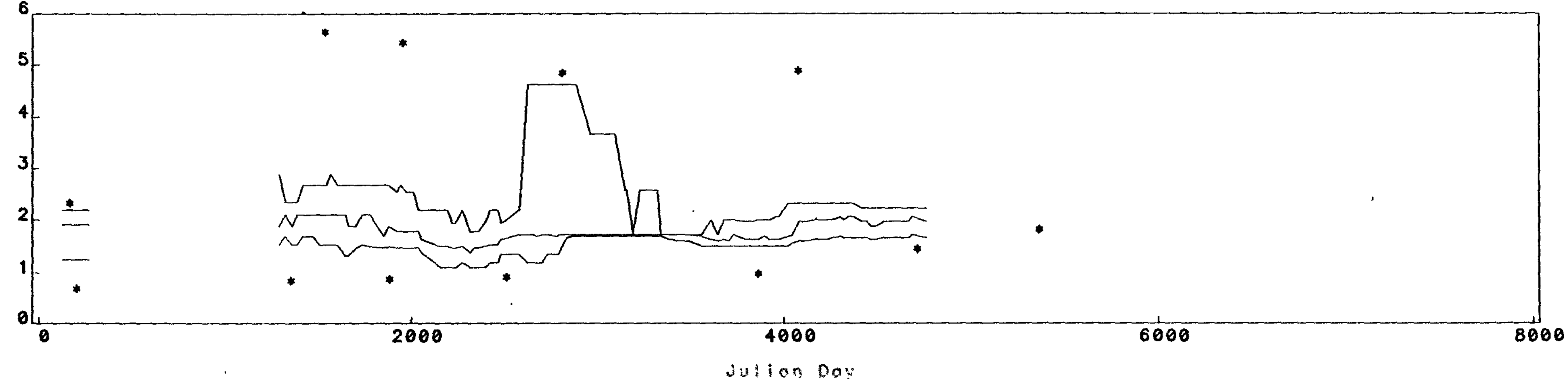
River no 18 Excess SO4 (Cl) +/- 12 months



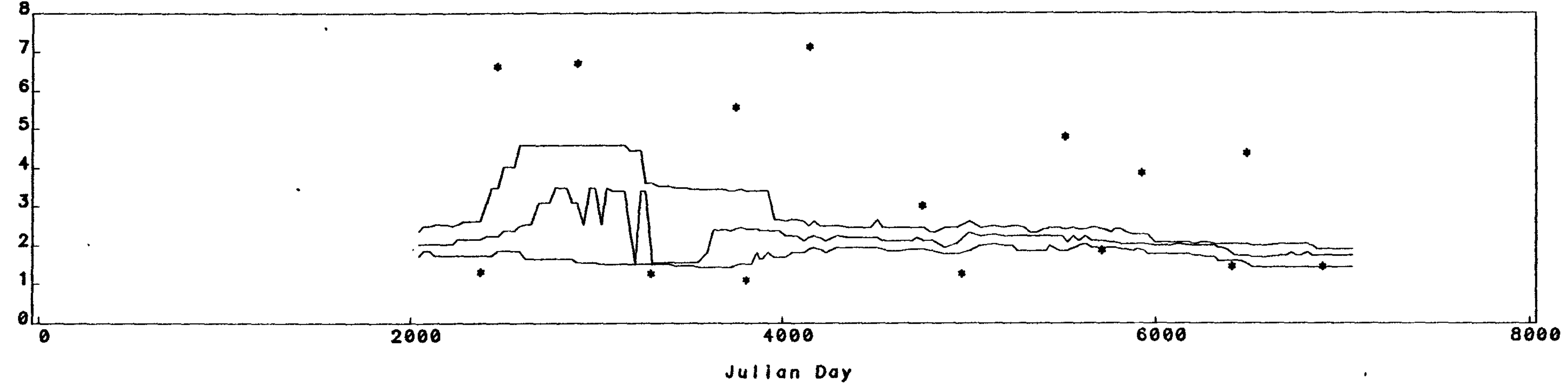
River no 19 Excess SO4 (Cl) +/- 12 months



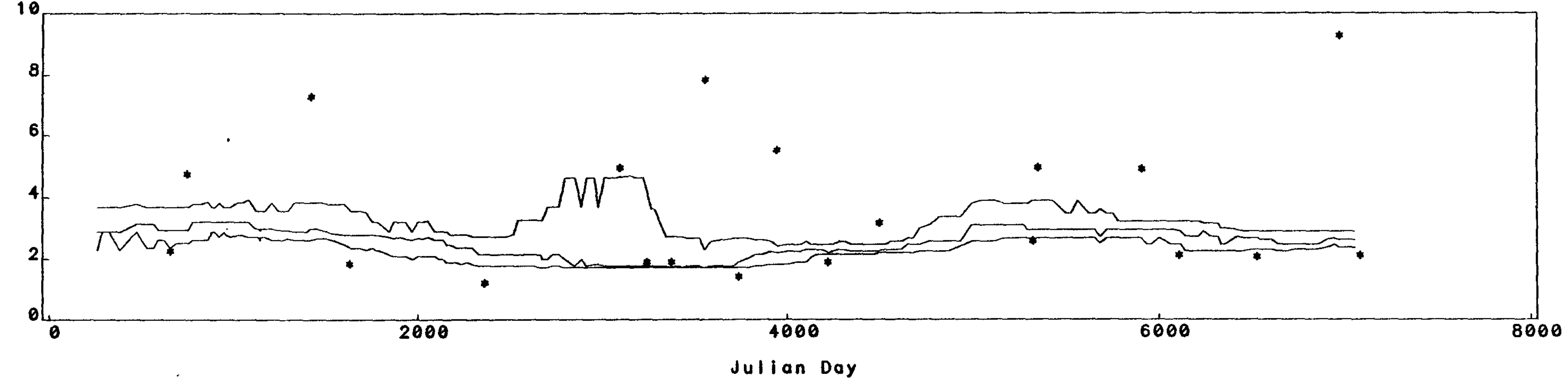
River no 20 Excess SO4 (Cl) +/- 12 months



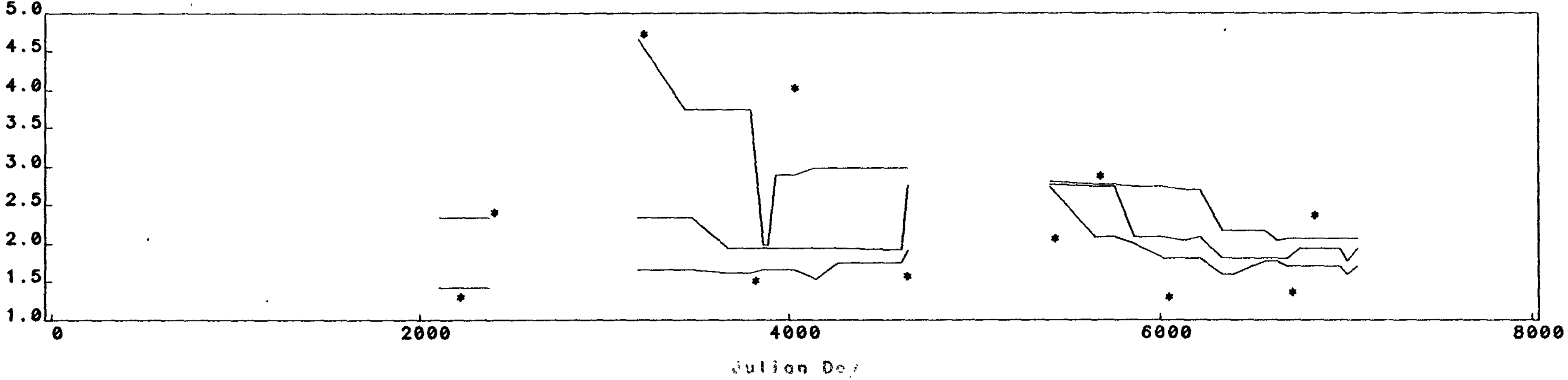
River no 21 Excess SO4 (Cl) +/- 12 months



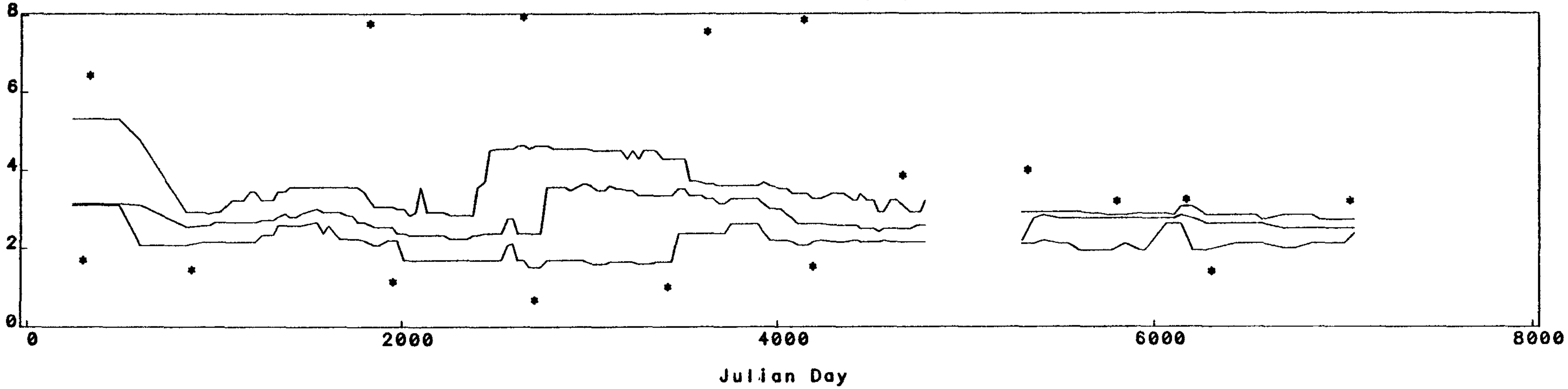
River no 22 Excess SO4 (Cl) +/- 12 months



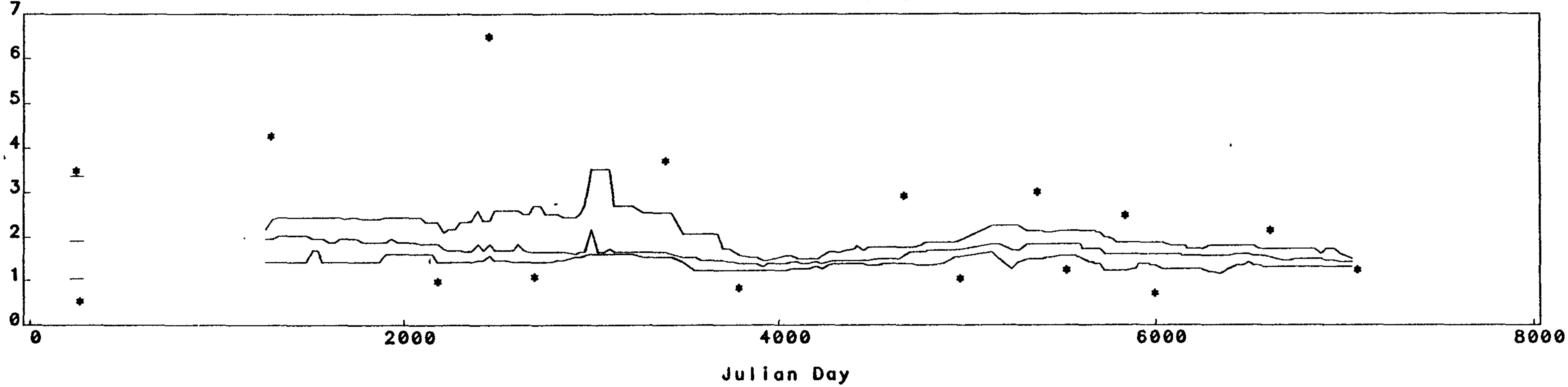
River no 23 Excess SO4 (Cl) +/- 12 months



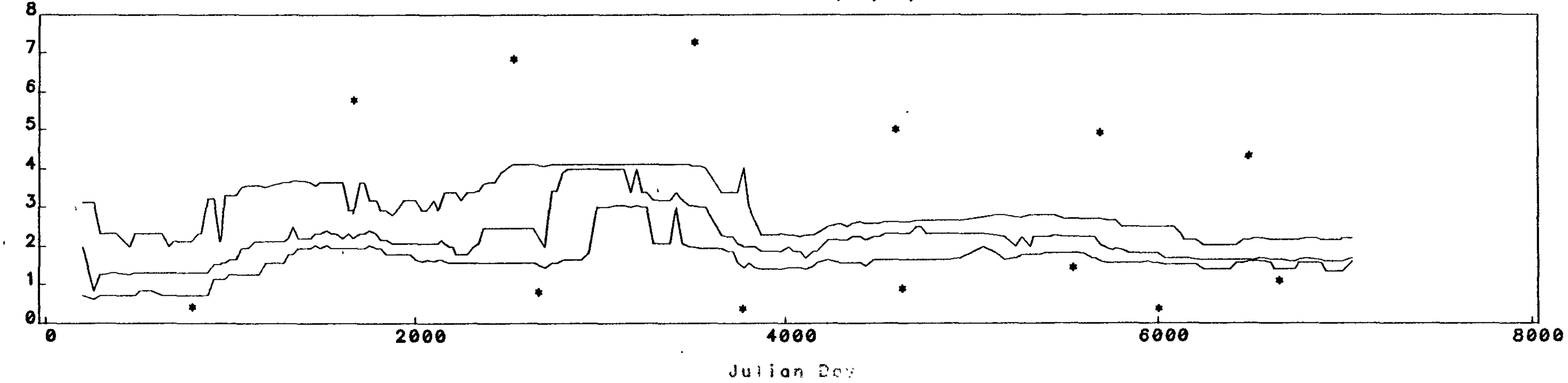
River no 25 Excess SO4 (Cl) +/- 12 months

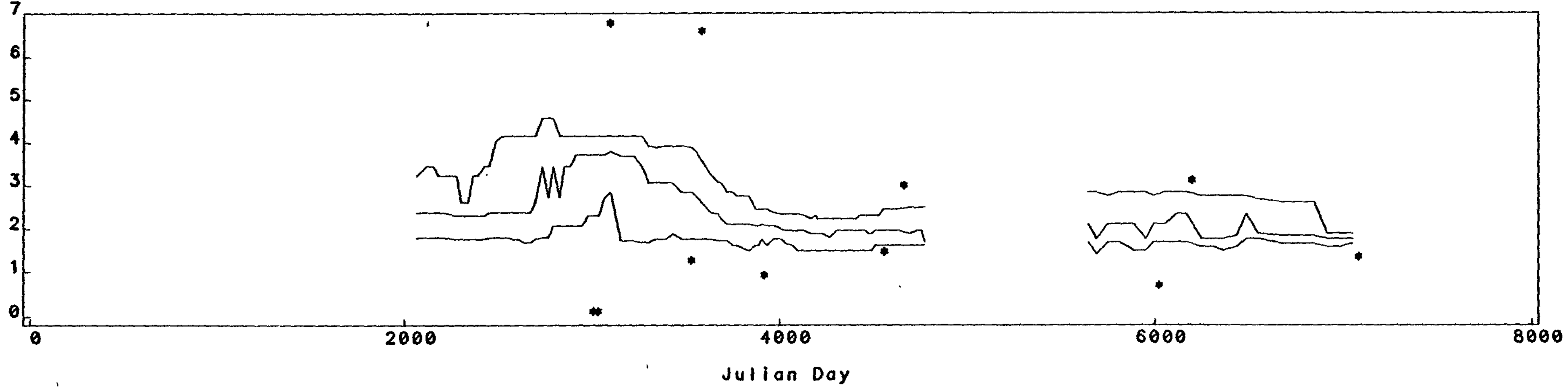


River no 26 Excess SO4 (Cl) +/- 12 months



River no 27 Excess SO4 (Cl) +/- 12 months



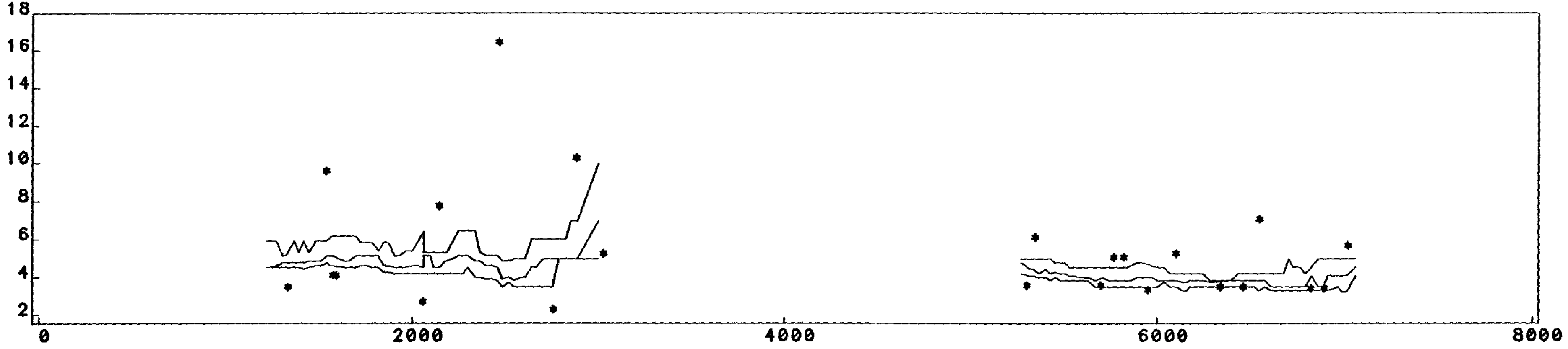


River no 28 Excess SO4 (Cl) +/- 12 months

Figure 11. Running boxplots of sulfate-MTB for the study rivers.

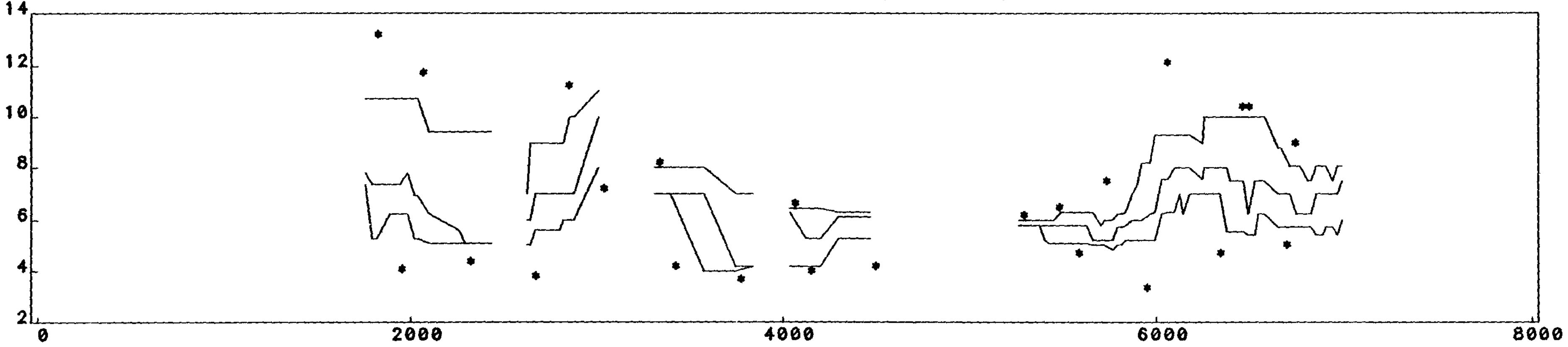
± 6 month

River no 1 SO4mtb (Sulphate MTB)



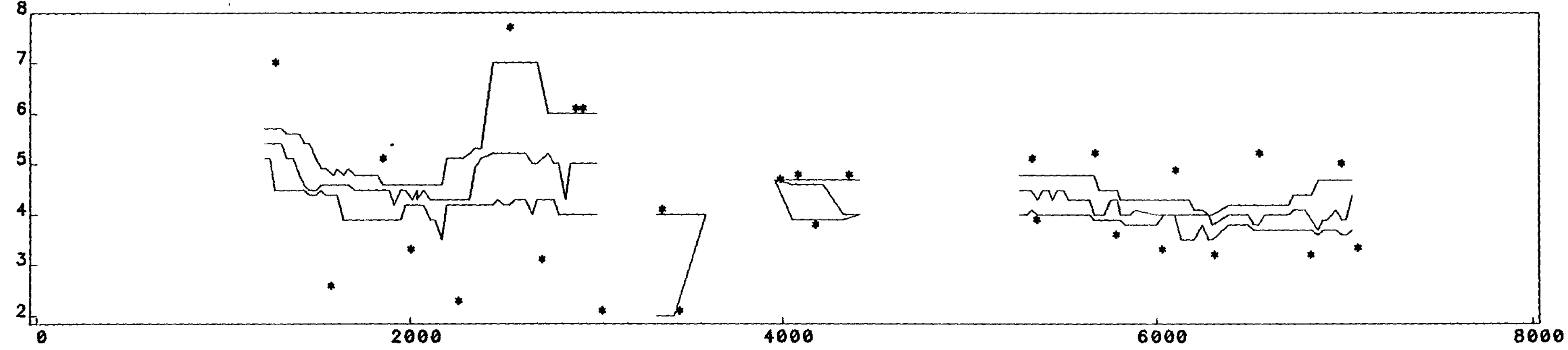
Julian Day

River no 2 SO4mtb (Sulphate MTB)



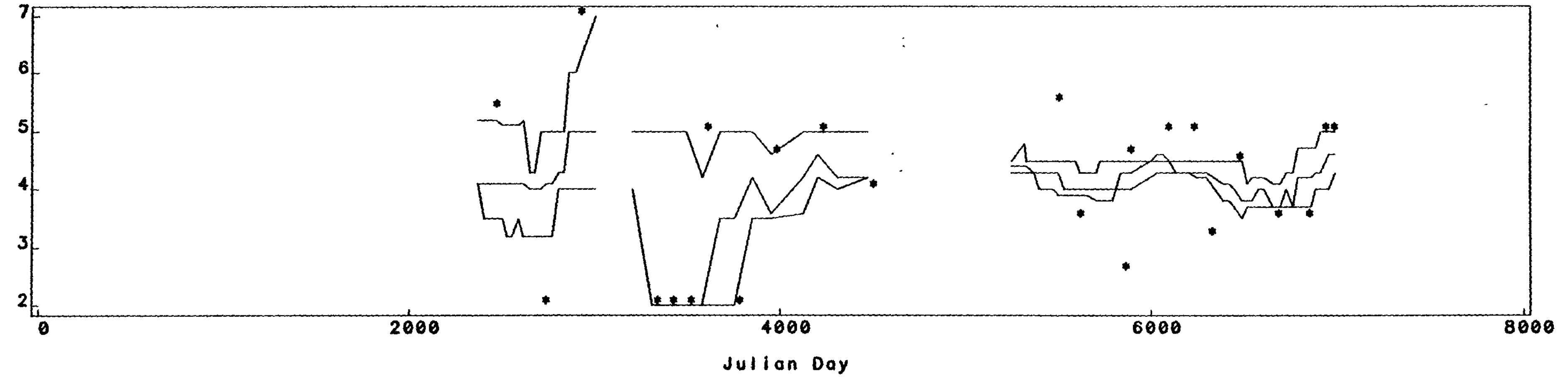
Julian Day

River no 3 SO4mtb (Sulphate MTB)

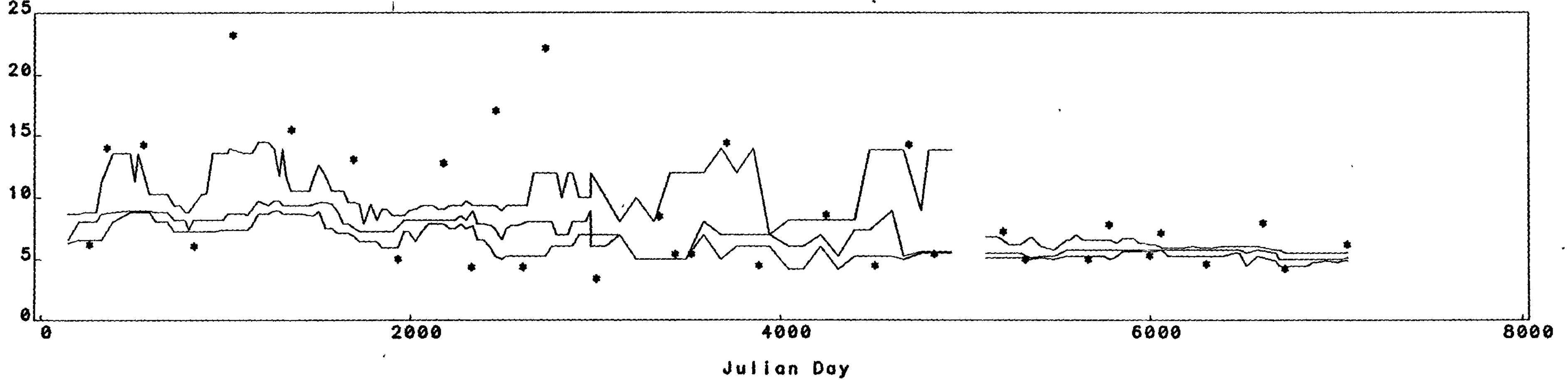


Julian Day

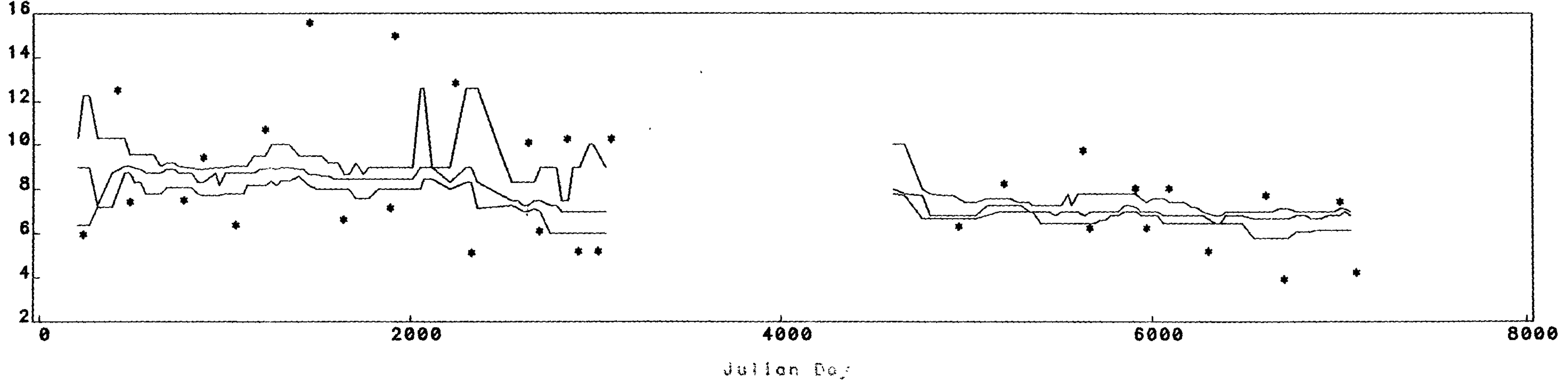
River no 4   SO4mtb (Sulphate MTB)

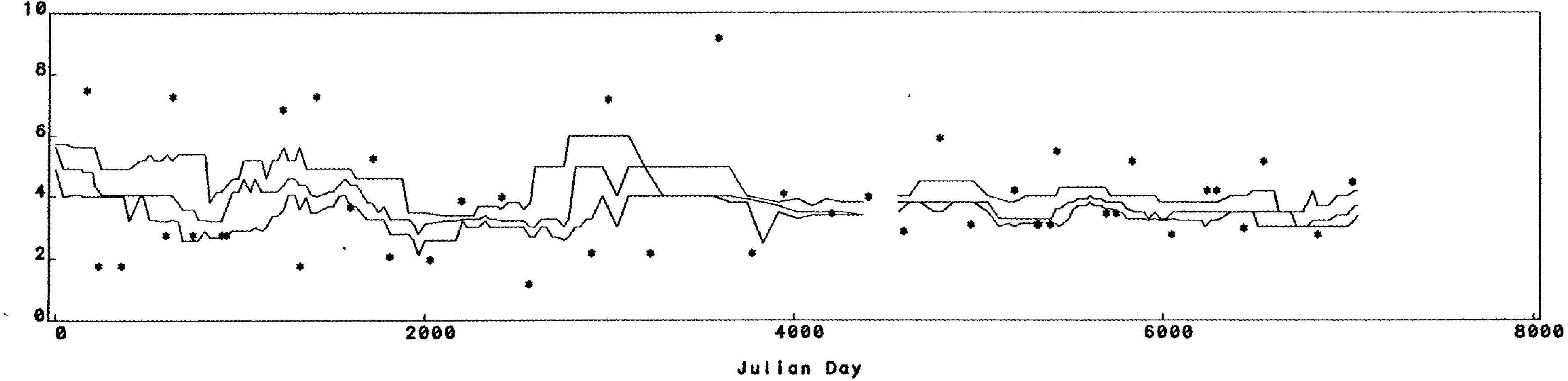


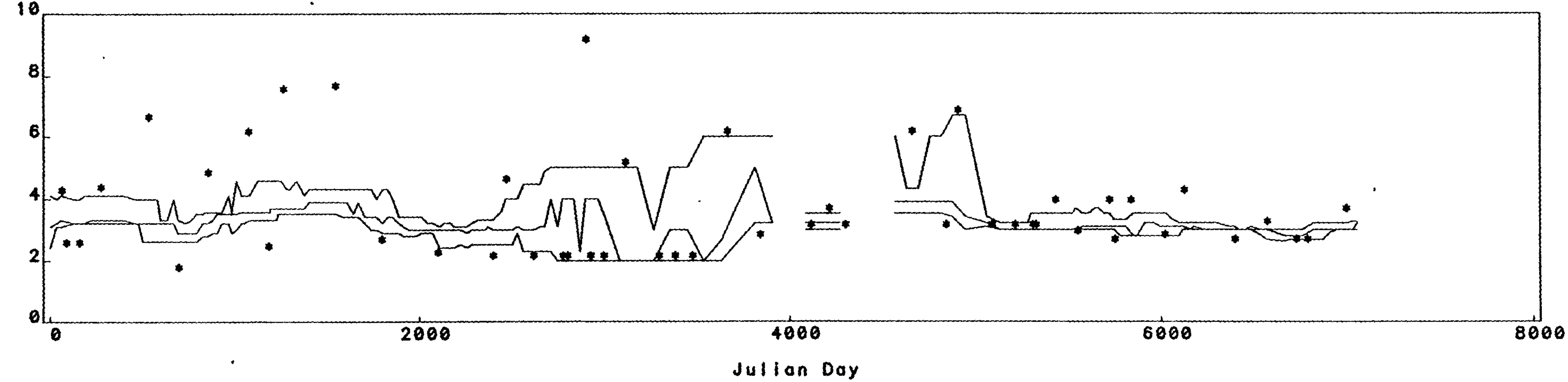
River no 5   SO4mtb (Sulphate MTB)

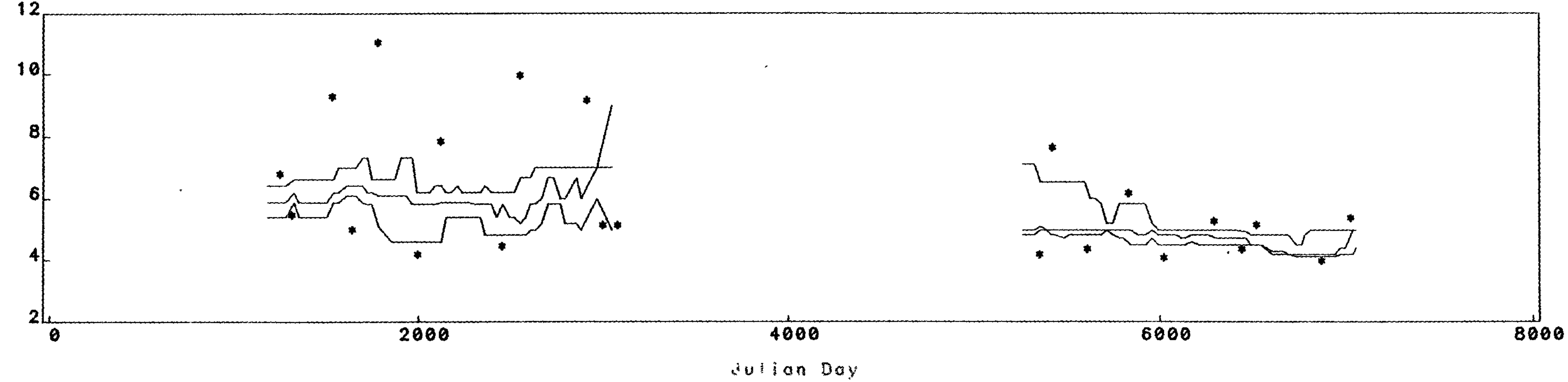


River no 6   SO4mtb (Sulphate MTB)




River no 7 SO4mtb (Sulphate MTB)


River no 8 SO4mtb (Sulphate MTB)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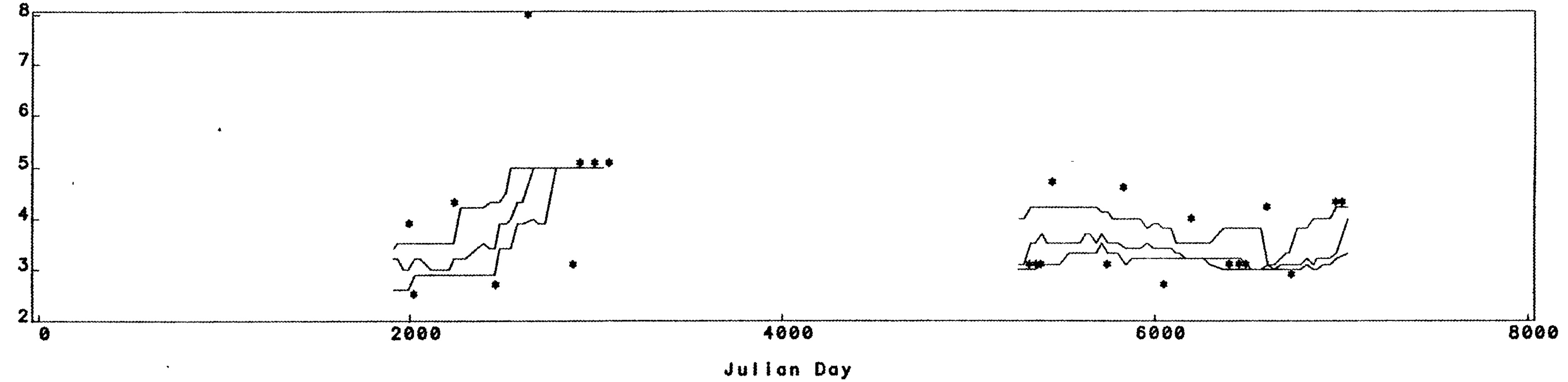
River no 10 SO4mtb (Sulphate MTB)



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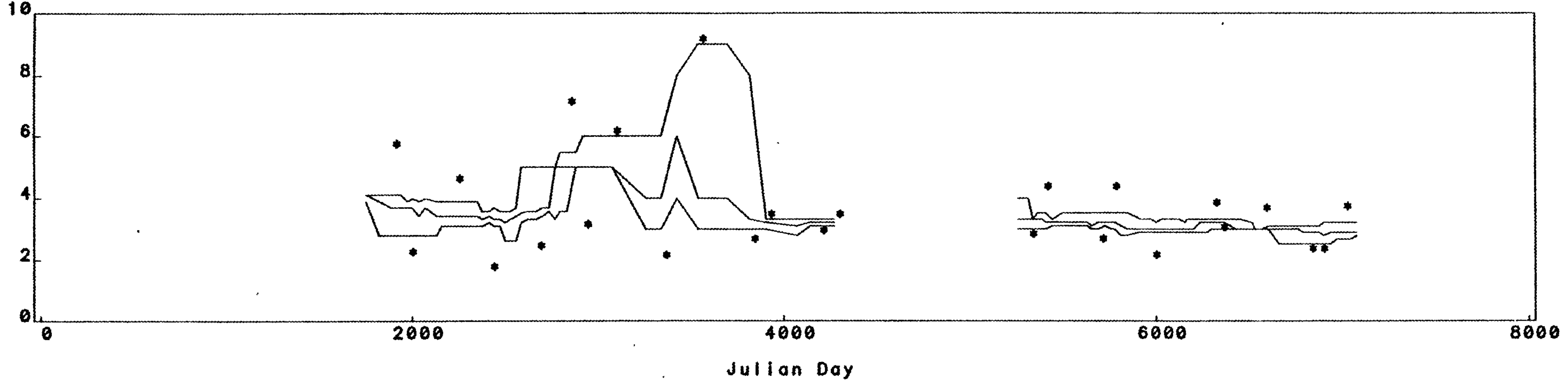
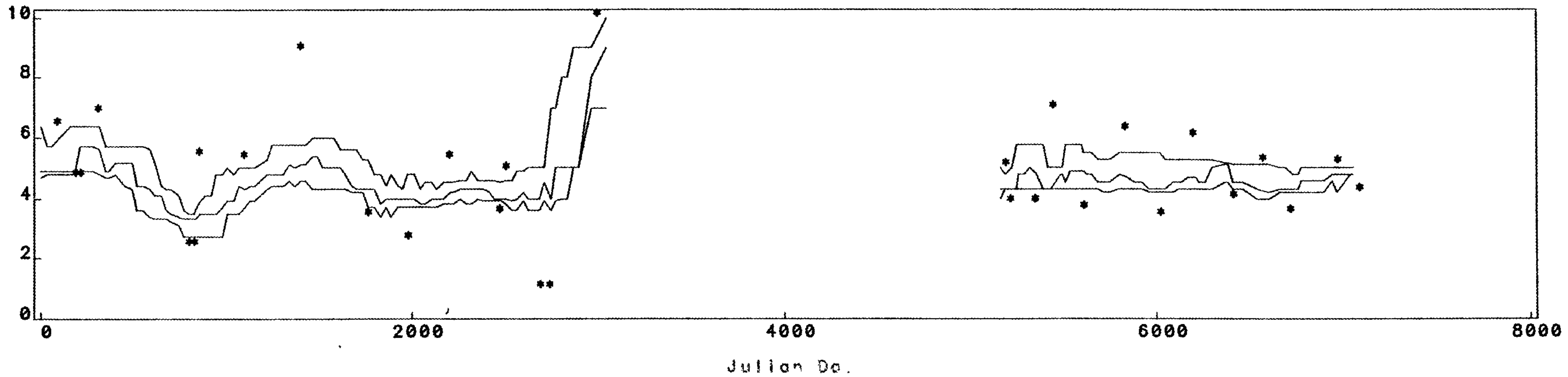
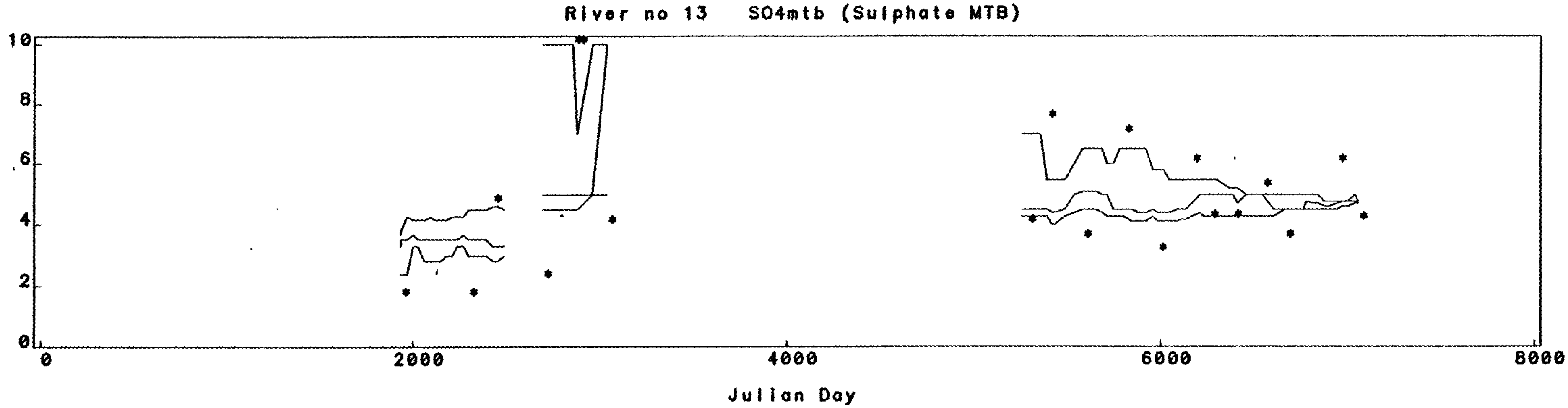
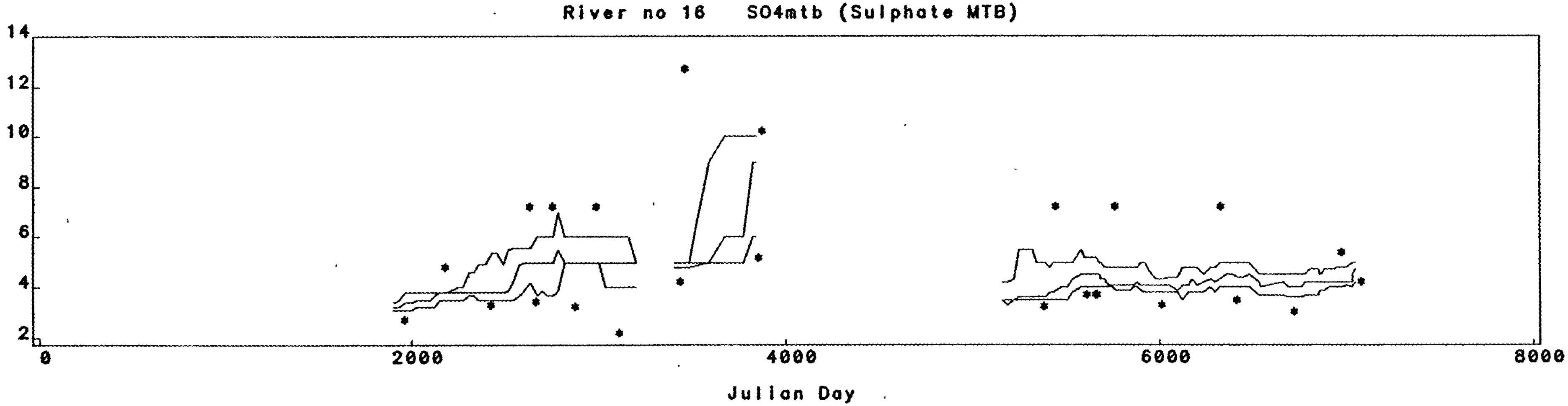
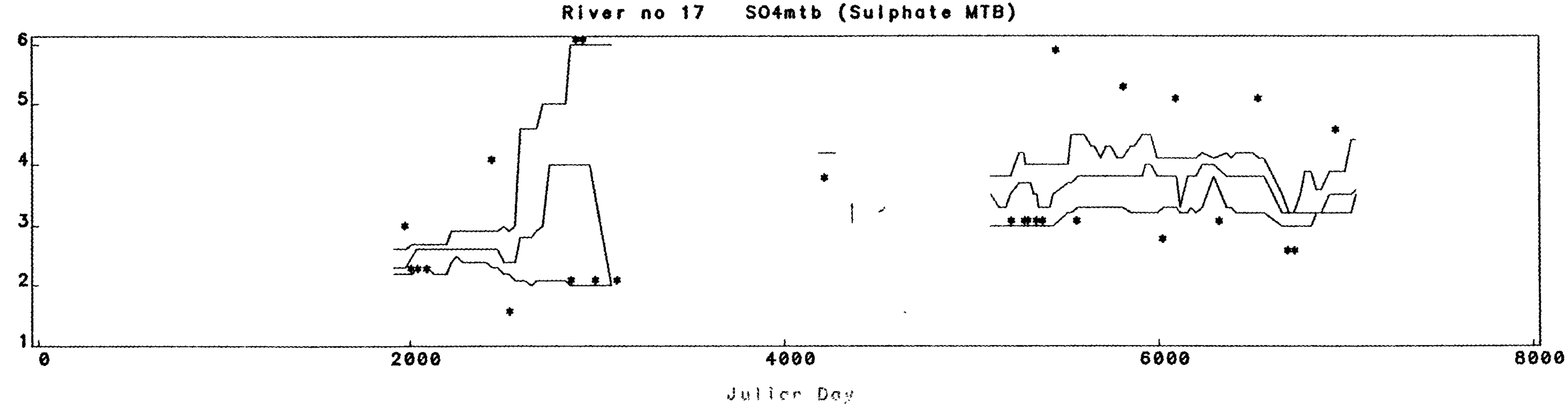


River no 12 SO4mtb (Sulphate MTB)

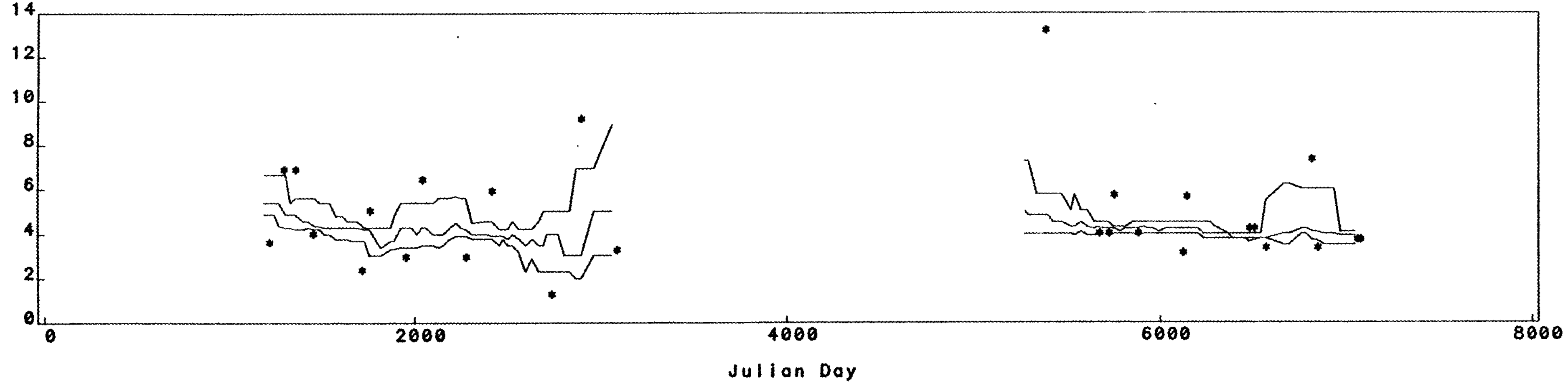



River no 13 SO4mtb (Sulphate MTB)
10
8
6
4
2
0
0
2000
4000
6000
8000
Julian Day


River no 16 SO4mtb (Sulphate MTB)
14
12
10
8
6
4
2
0
2000
4000
6000
8000
Julian Day


River no 17 SO4mtb (Sulphate MTB)
6
5
4
3
2
1
0
2000
4000
6000
8000
Julian Day

River no 18 SO4mtb (Sulphate MTB)



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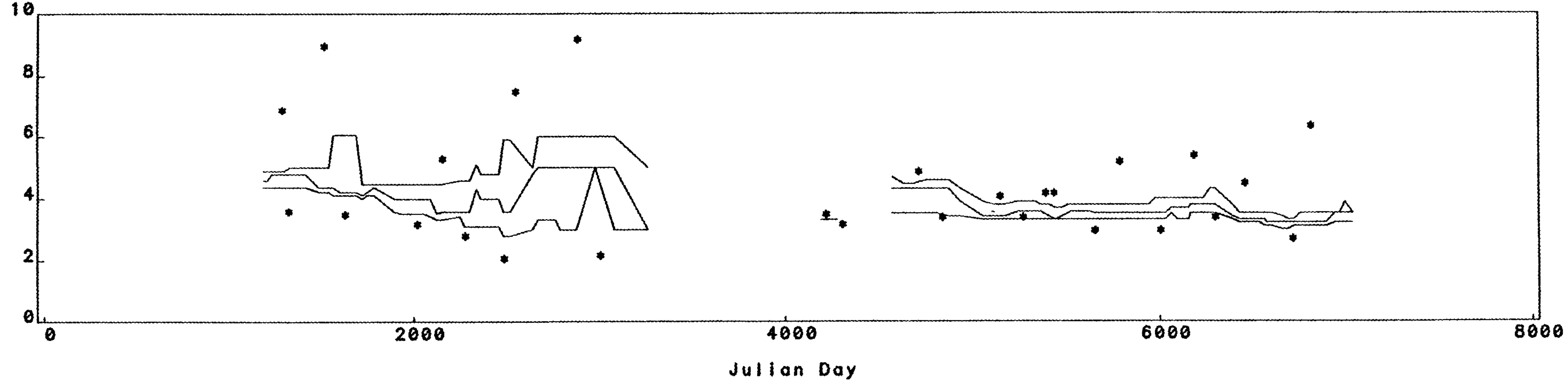
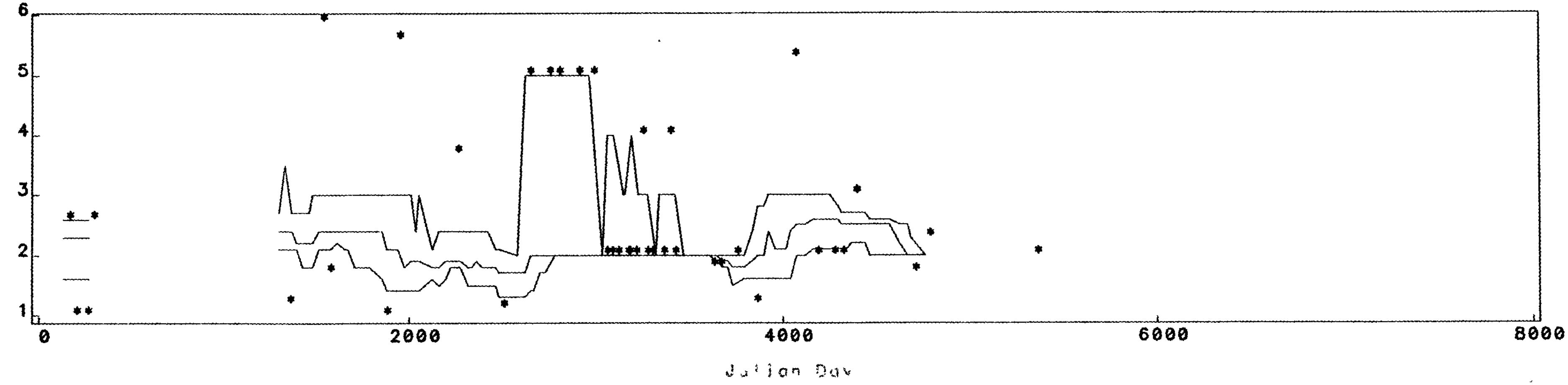
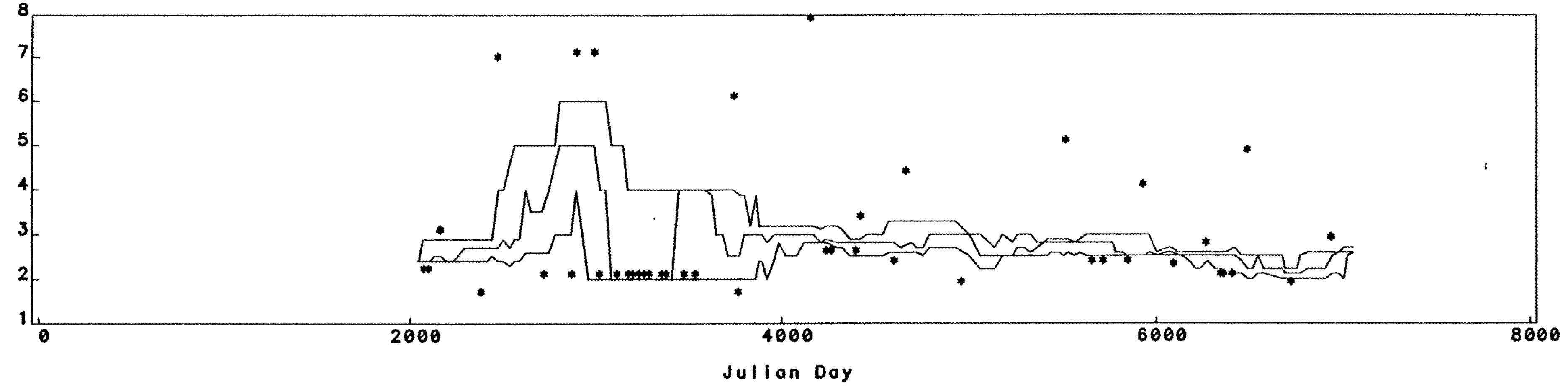


River no 20 SO4mtb (Sulphate MTB)



River no 21 SO4mtb (Sulphate MTB)



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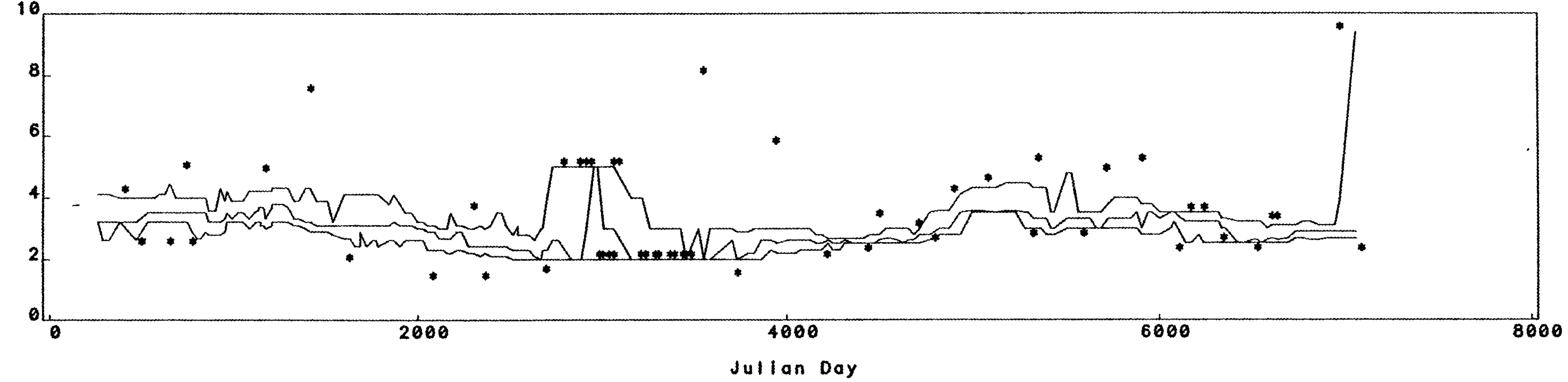

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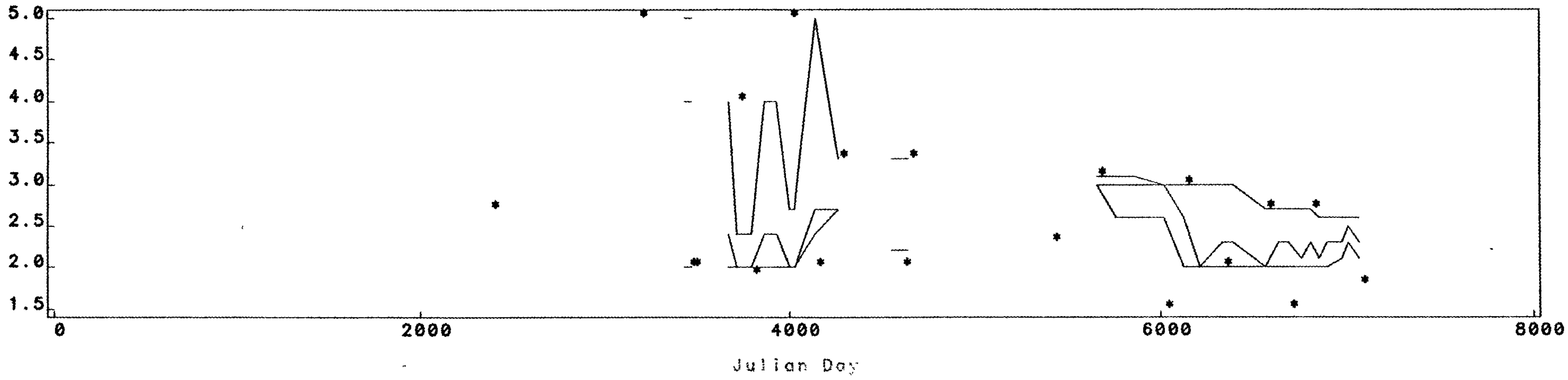

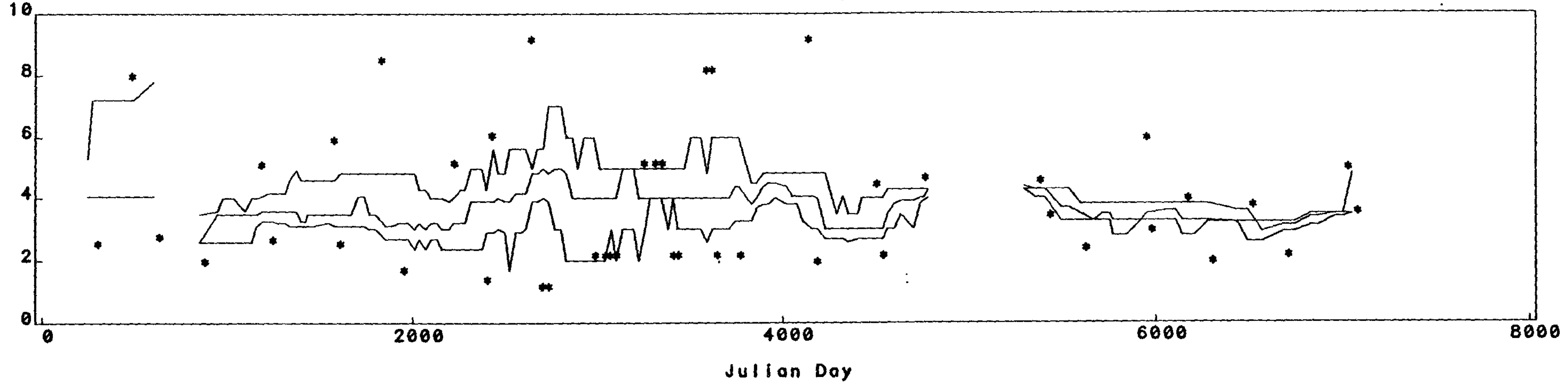
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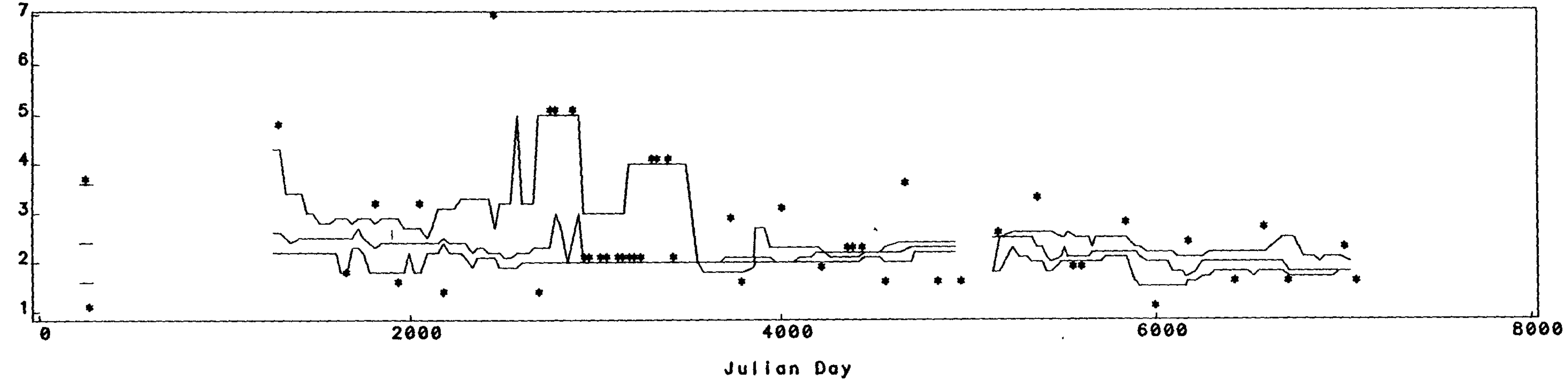
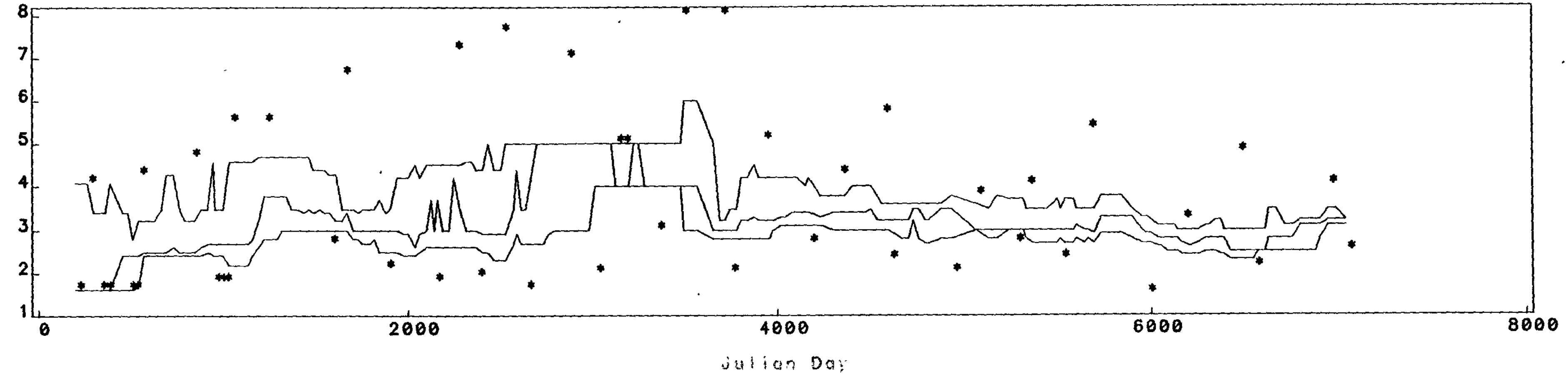
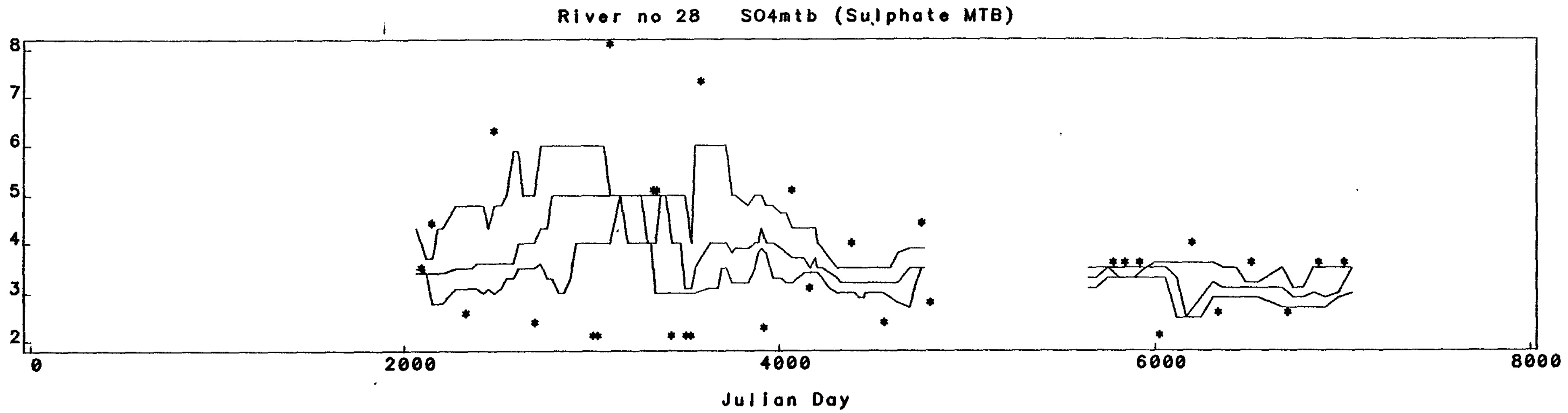
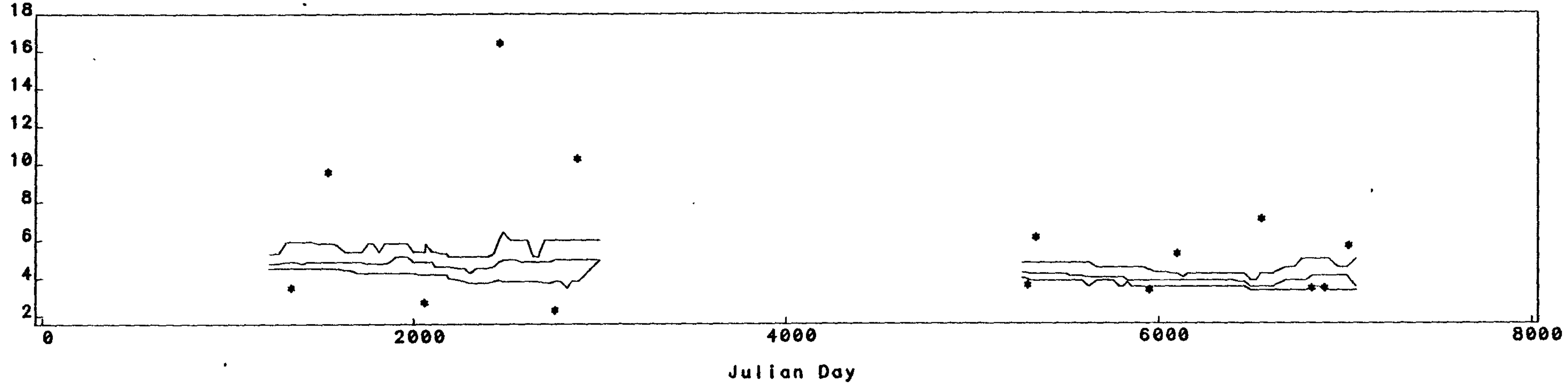

River no 26 SO4mtb (Sulphate MTB)


River no 27 SO4mtb (Sulphate MTB)

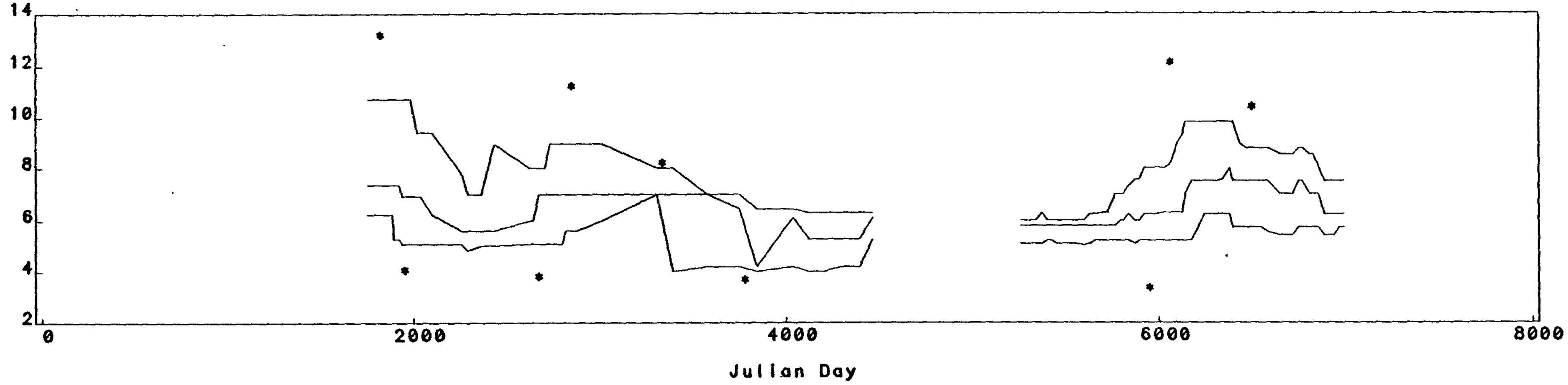


River no 28 SO4mtb (Sulphate MTB)

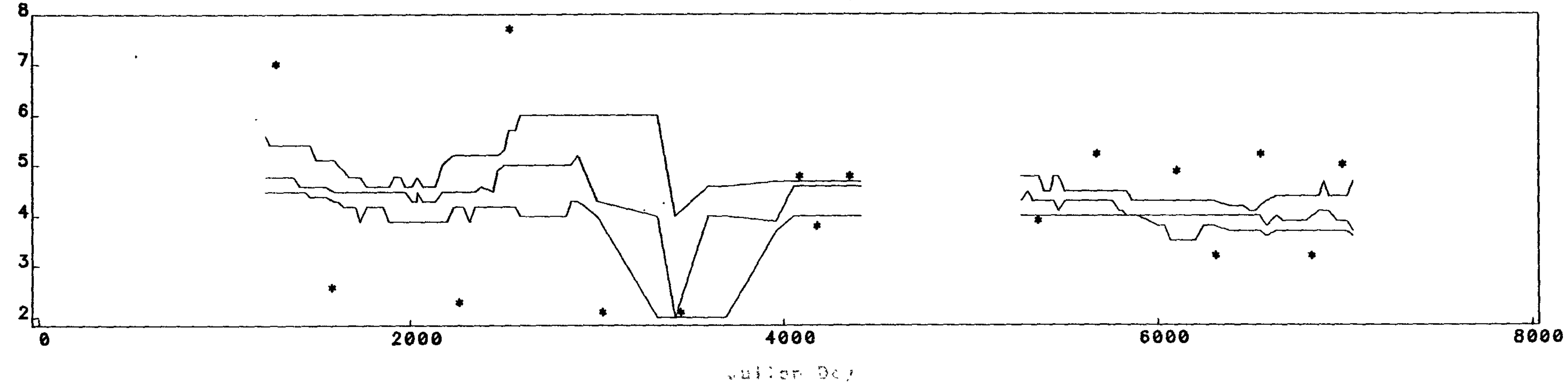
River no 1 SO4 MTB +/- 12 months



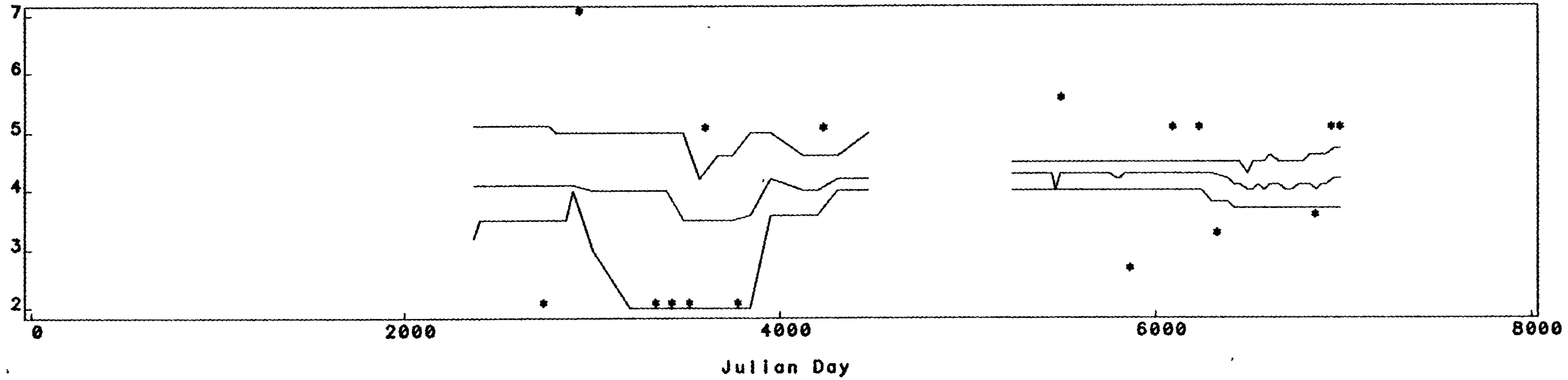
River no 2 SO4 MTB +/- 12 months



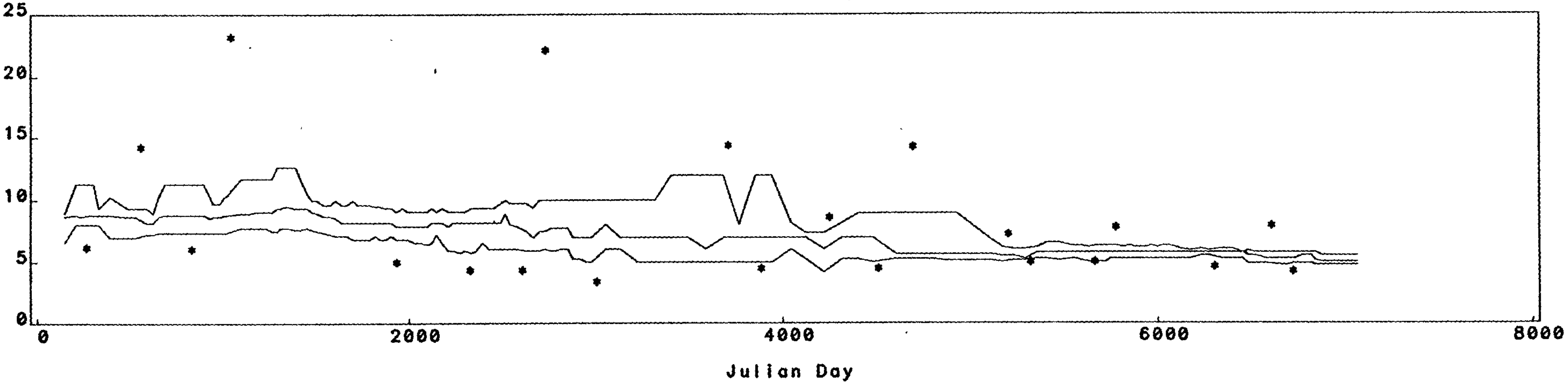
River no 3 SO4 MTB +/- 12 months



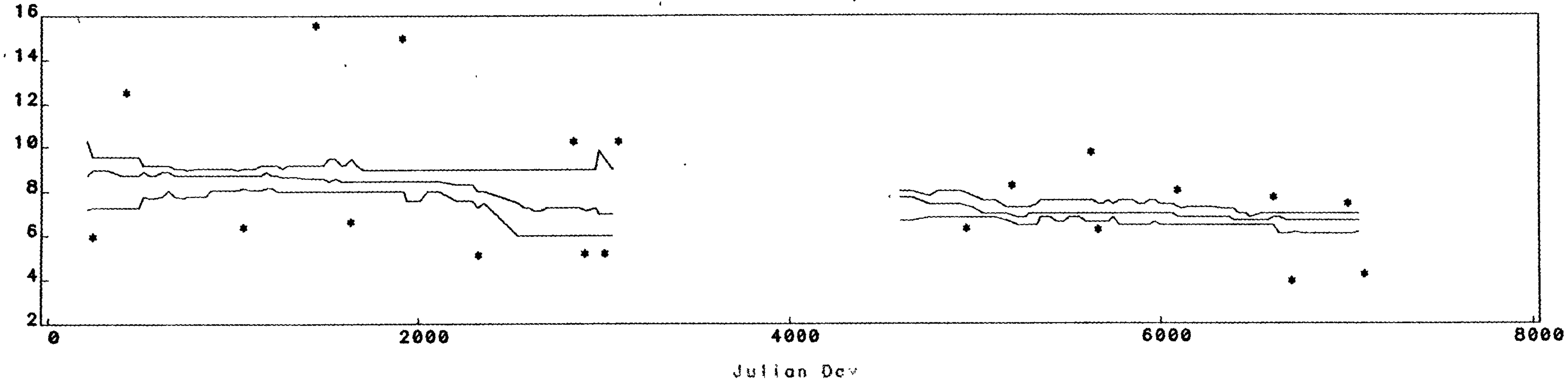
River no 4 SO4 MTB +/- 12 months

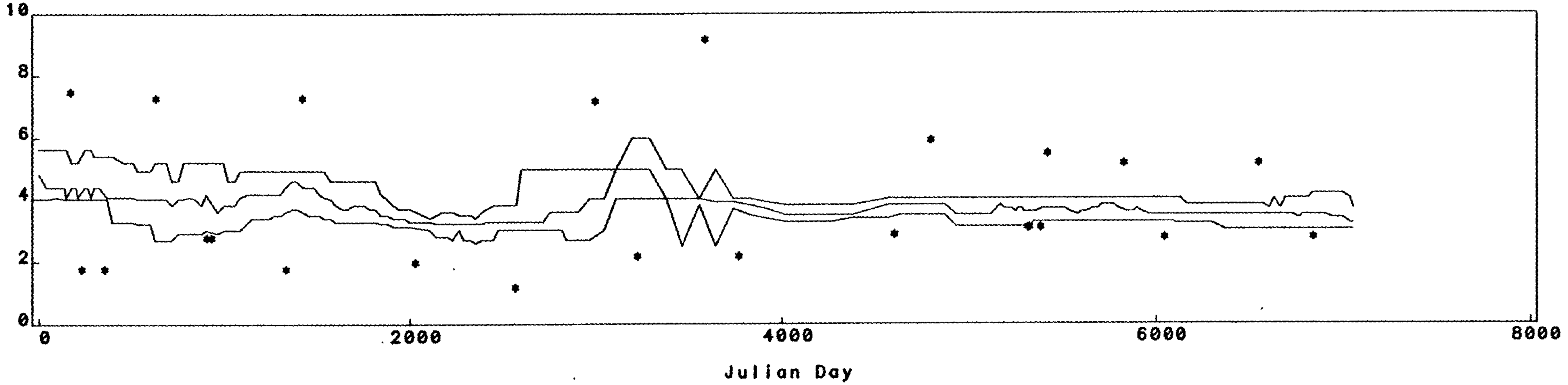


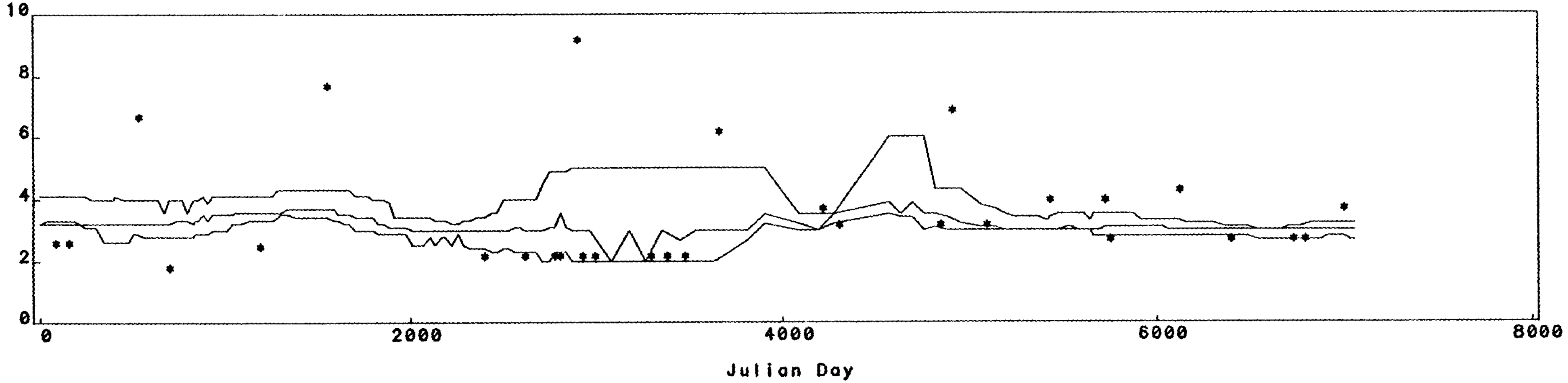
River no 5 SO4 MTB +/- 12 months

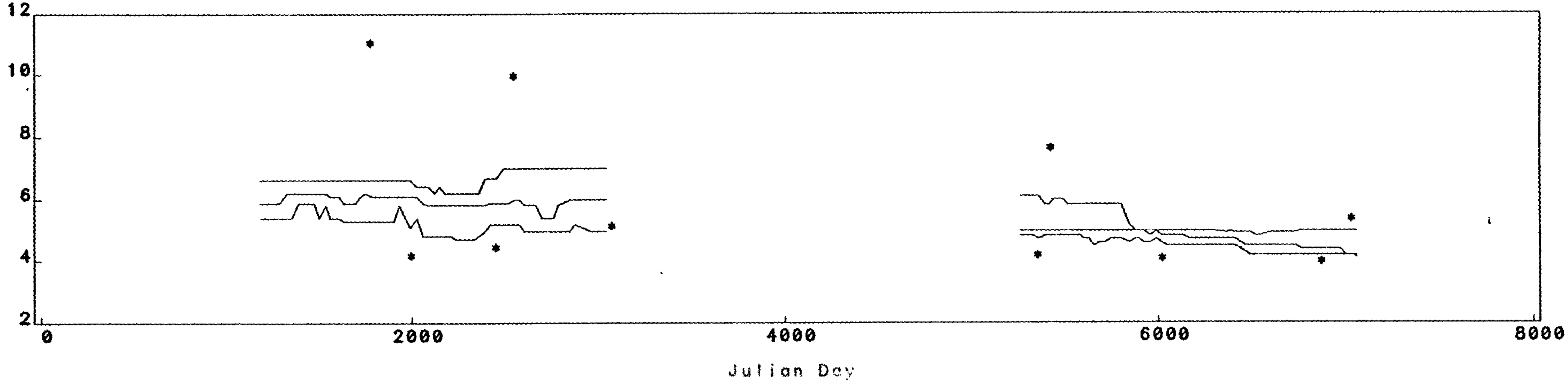


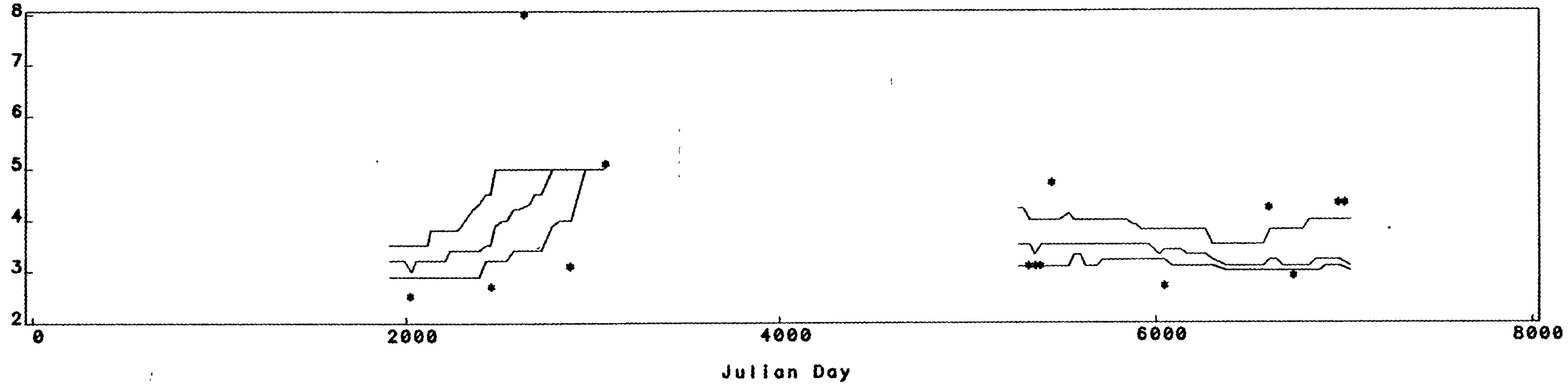
River no 6 SO4 MTB +/- 12 months

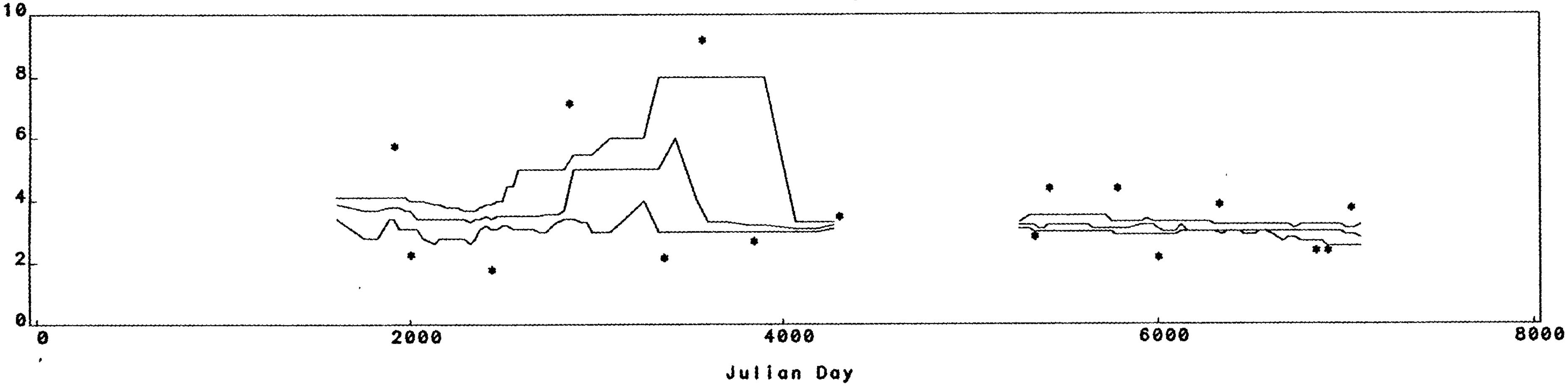


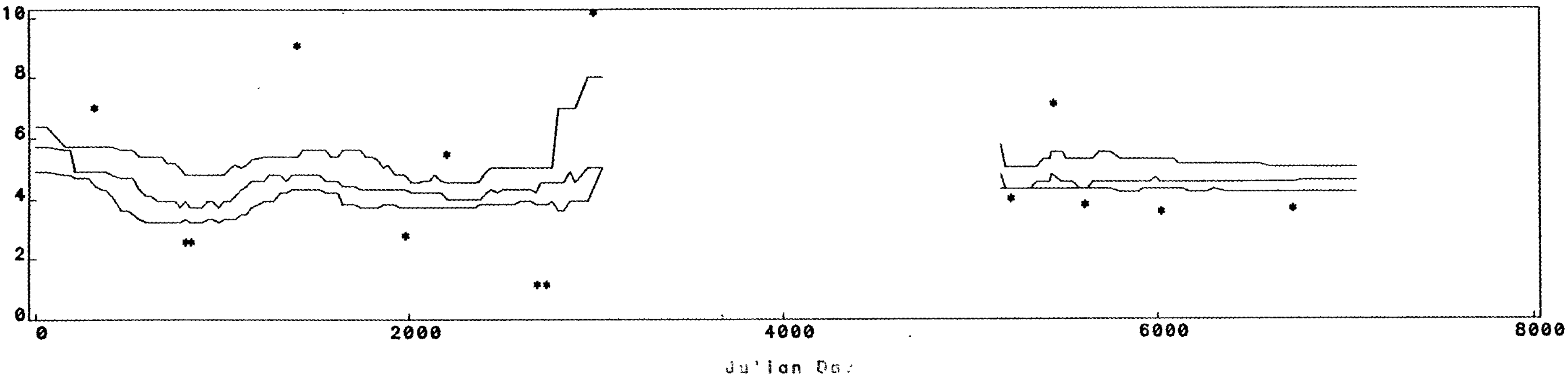

River no 7 SO4 MTB +/- 12 months


River no 8 SO4 MTB +/- 12 months

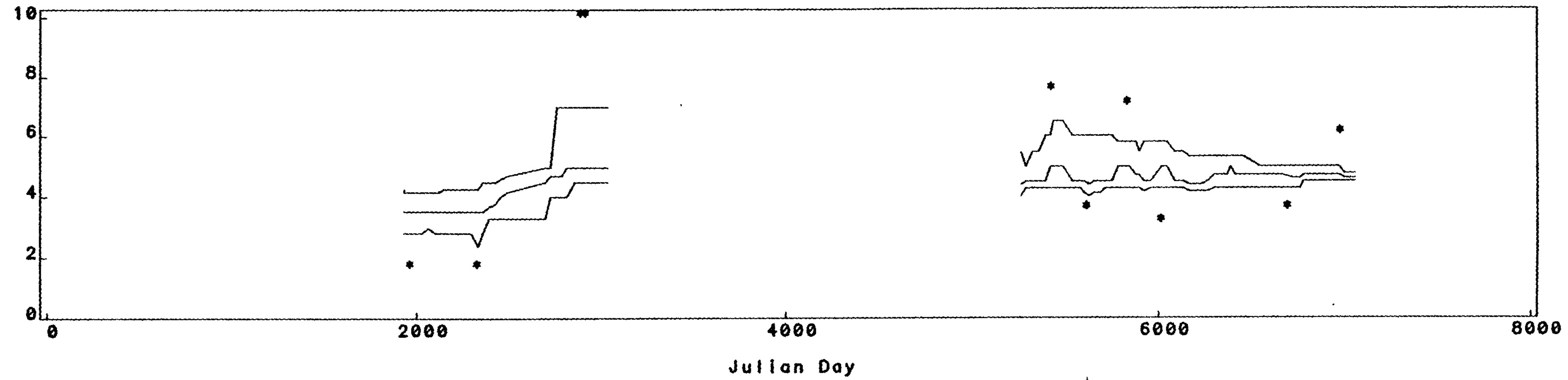

River no 9 SO4 MTB +/- 12 months


River no 10 SO4 MTB +/- 12 months

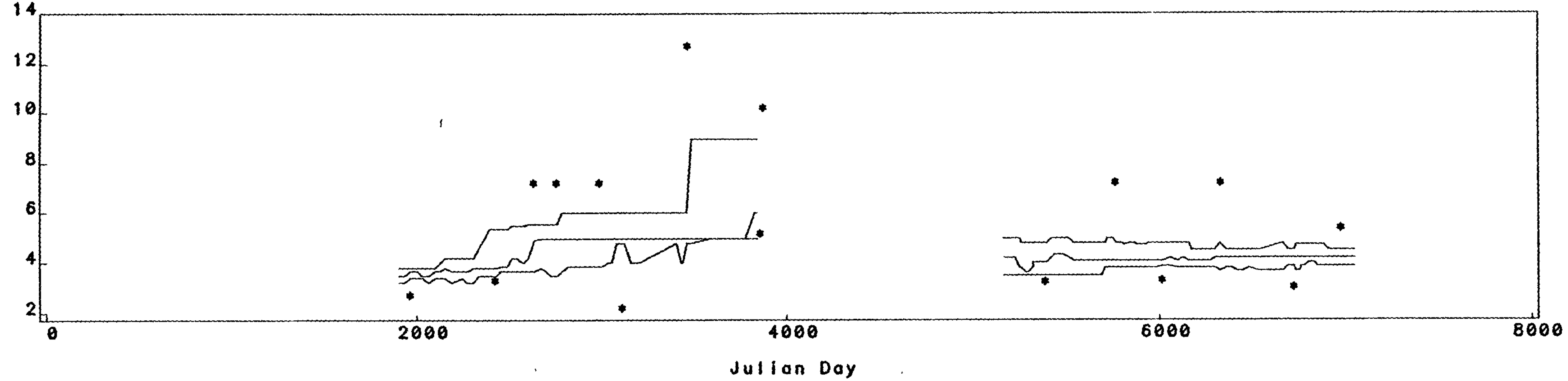

River no 11 SO4 MTB +/- 12 months


River no 12 SO4 MTB +/- 12 months

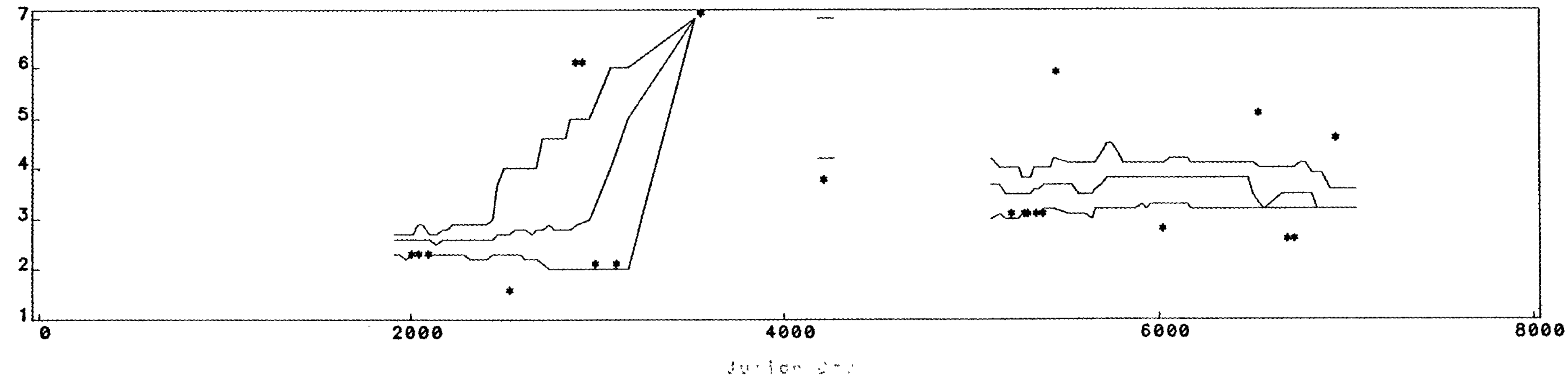
River no 13 SO4 MTB +/- 12 months

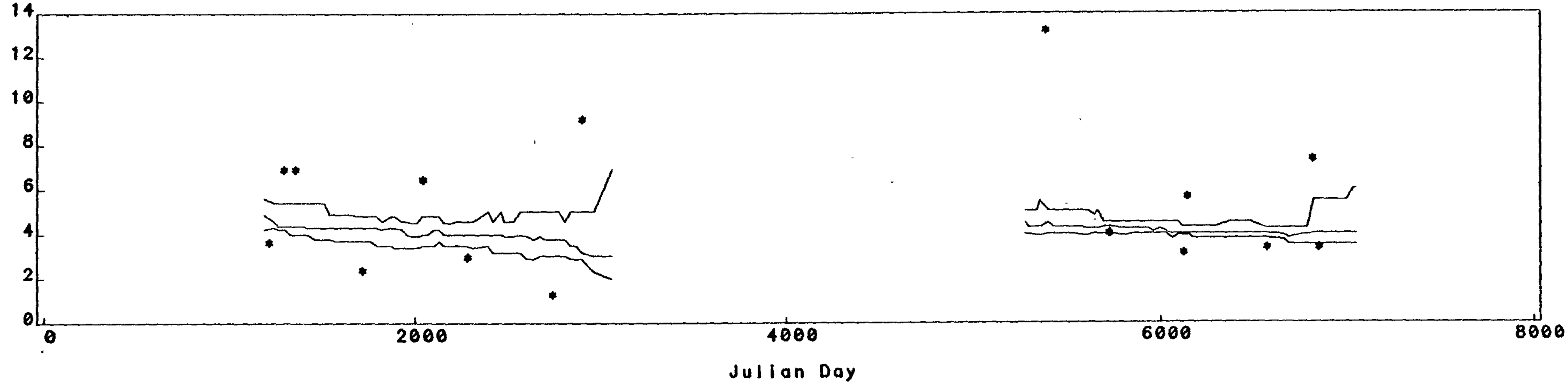


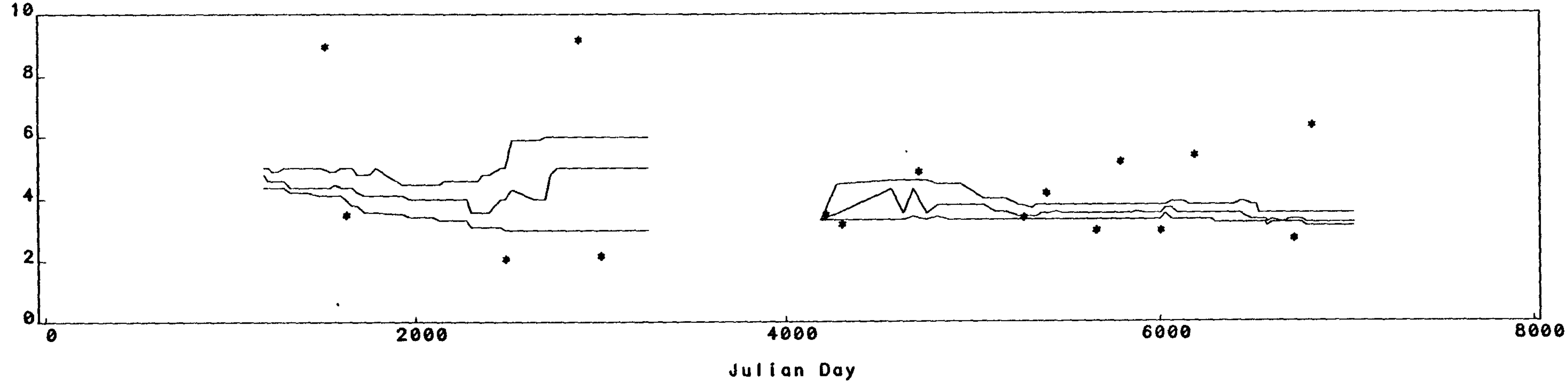
River no 16 SO4 MTB +/- 12 months

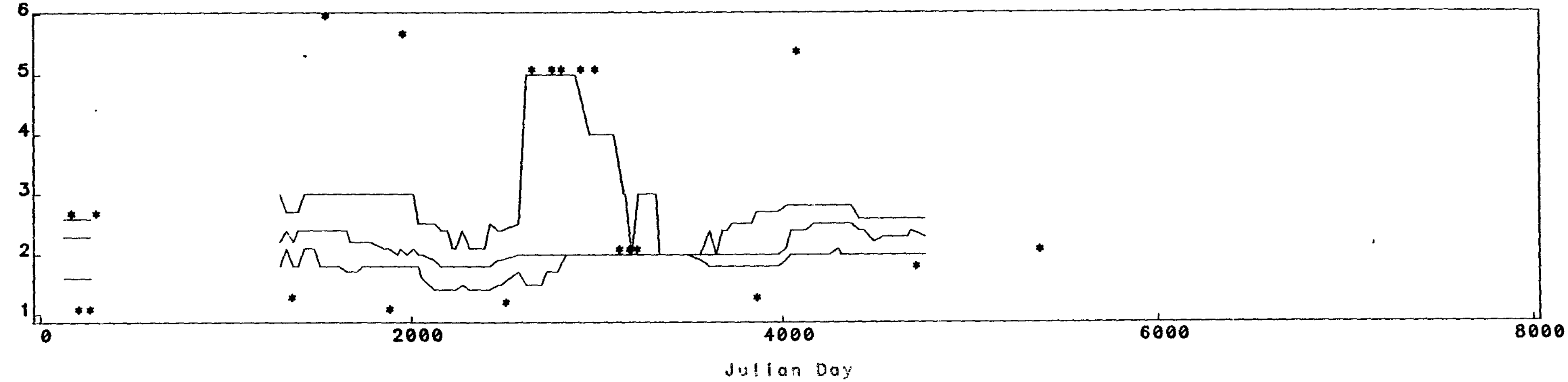


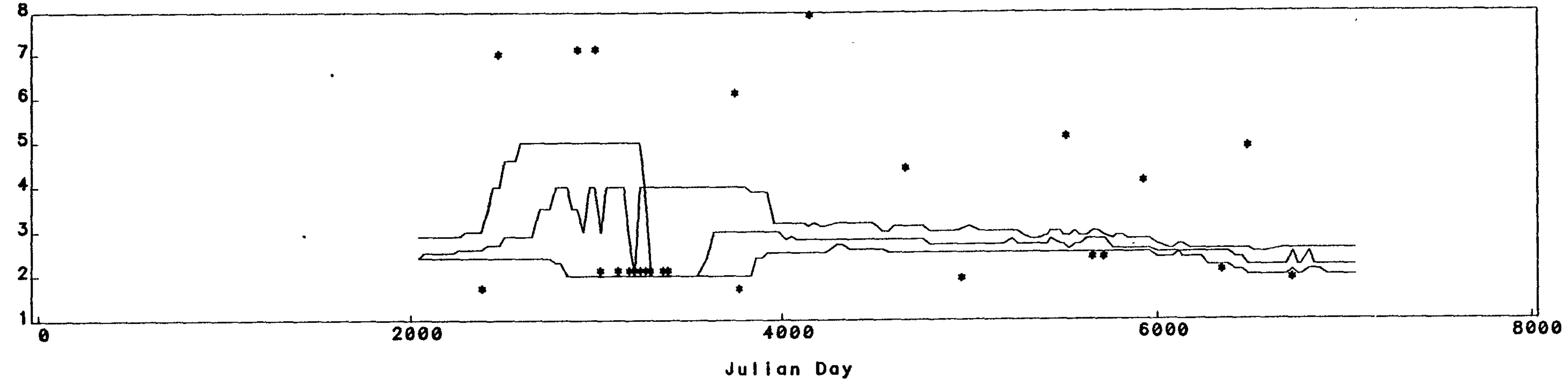
River no 17 SO4 MTB +/- 12 months

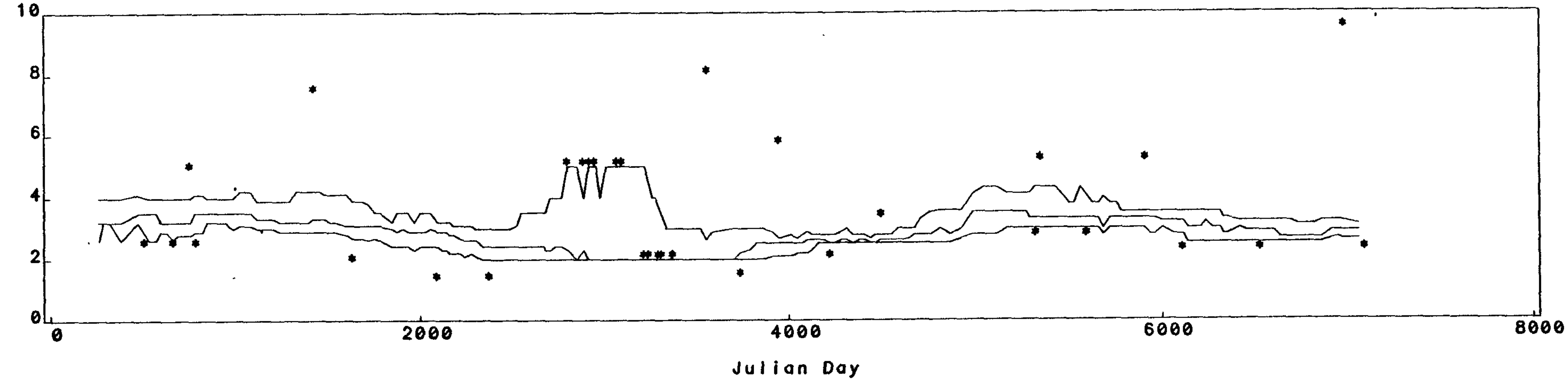


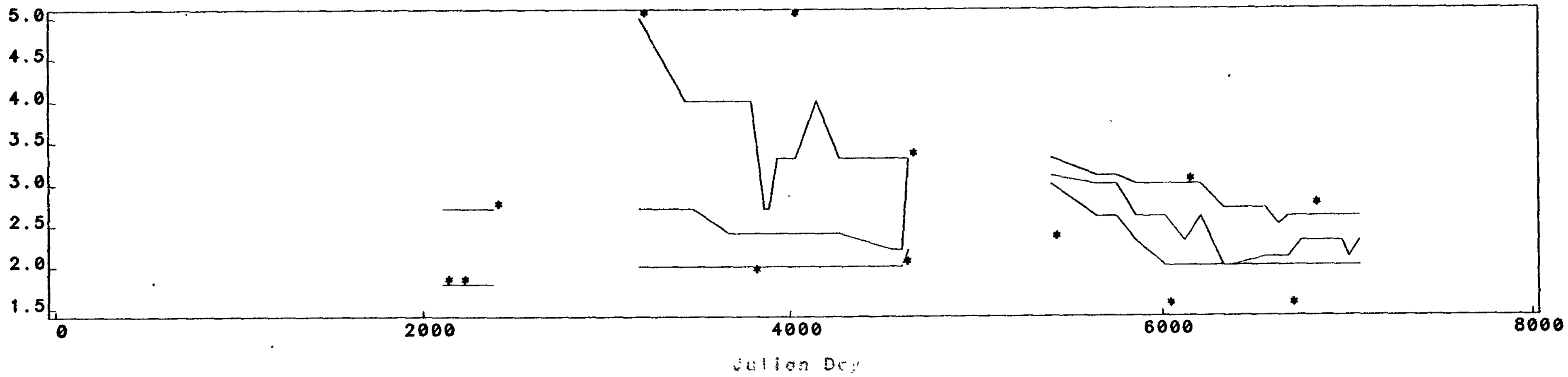

River no 18 SO4 MTB +/- 12 months


River no 19 SO4 MTB +/- 12 months

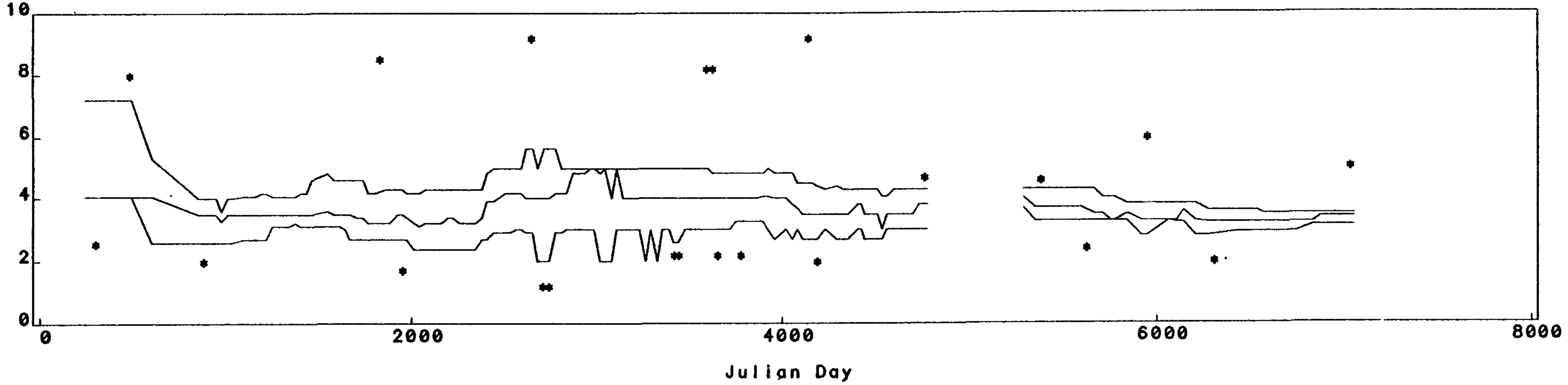

River no 20 SO4 MTB +/- 12 months


River no 21 SO4 MTB +/- 12 months

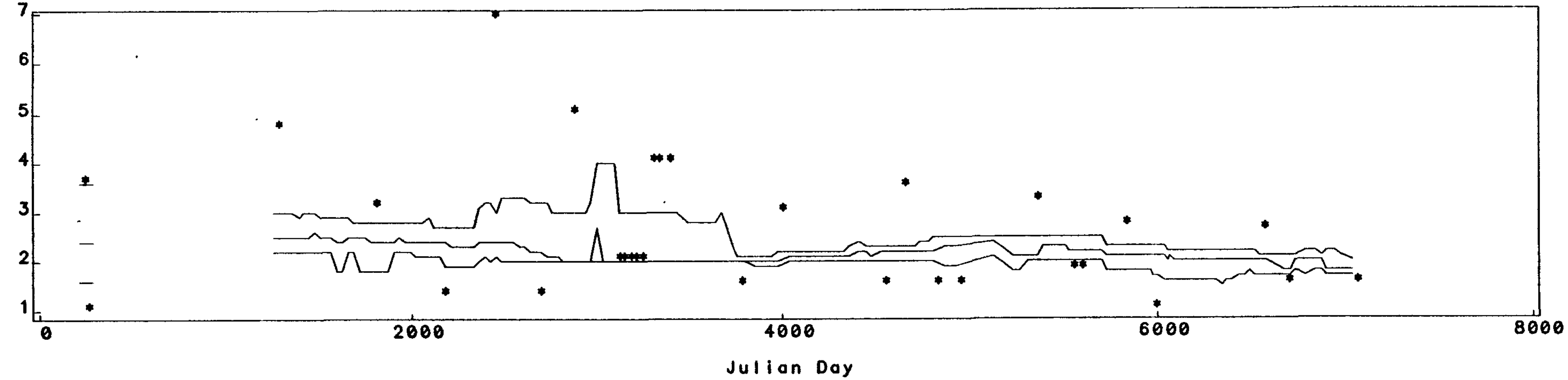

River no 22 SO4 MTB +/- 12 months


River no 23 SO4 MTB +/- 12 months

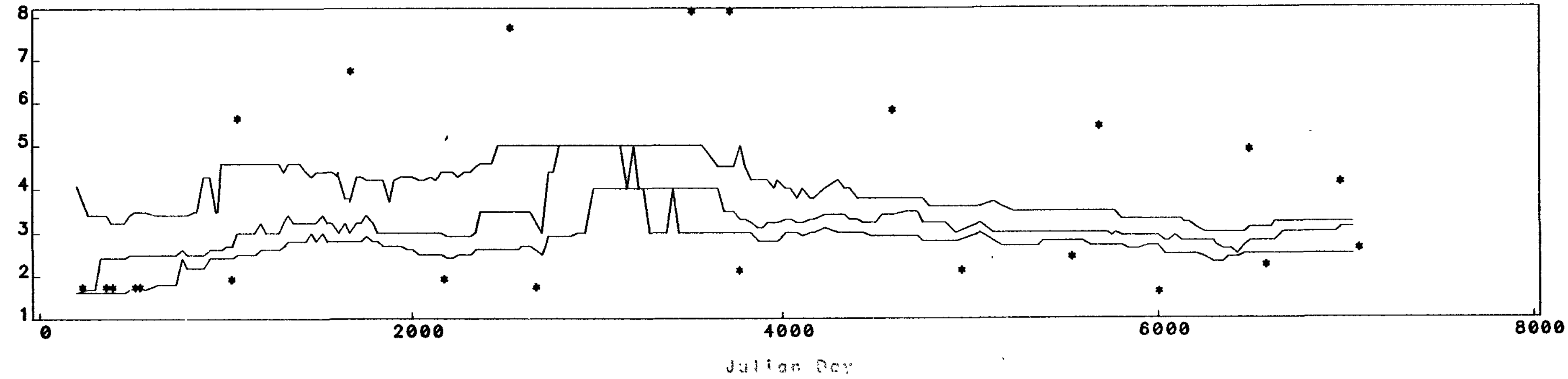
River no 25 SO4 MTB +/- 12 months



River no 26 SO4 MTB +/- 12 months



River no 27 SO4 MTB +/- 12 months



River no 28 SO4 MTB +/- 12 months

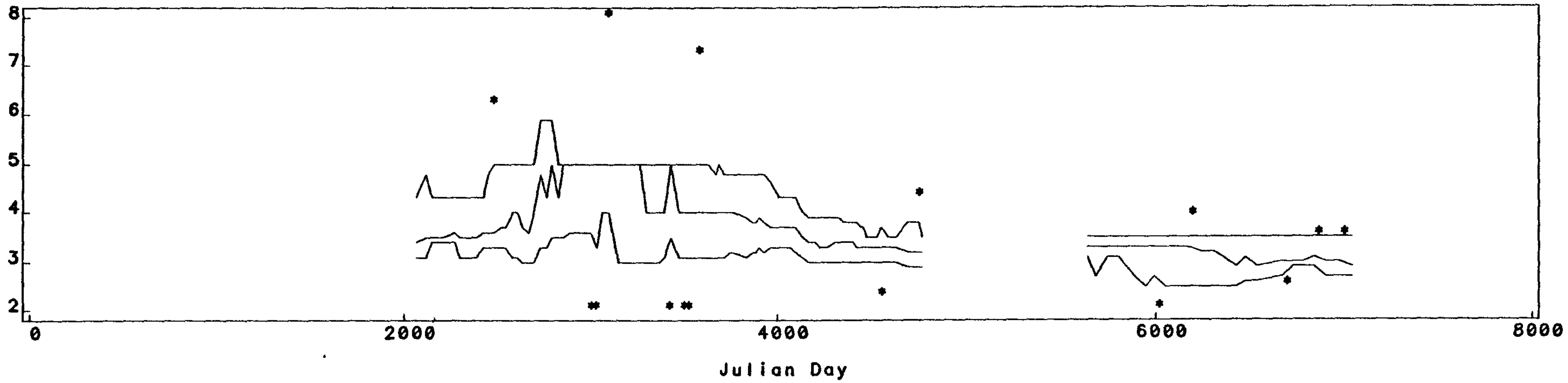
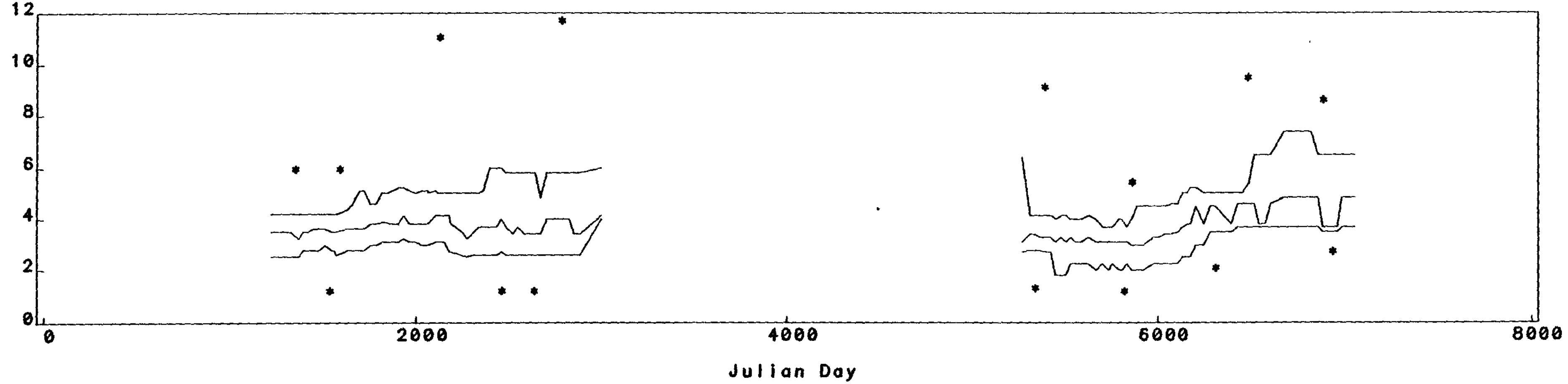
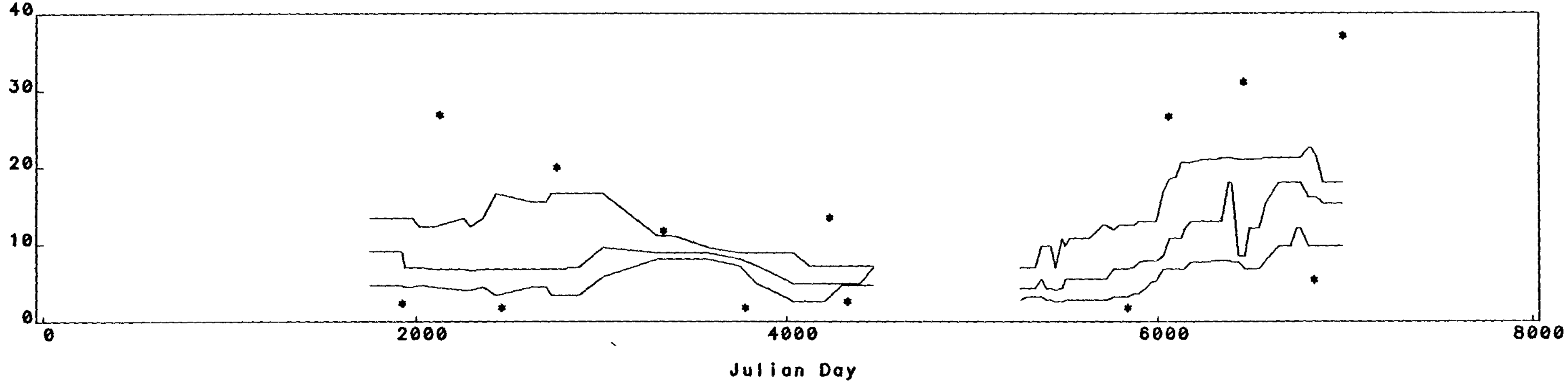


Figure 12. Running boxplots of total alkalinity for the study rivers.

+/- 6 months


River no 1 Total Alkalinity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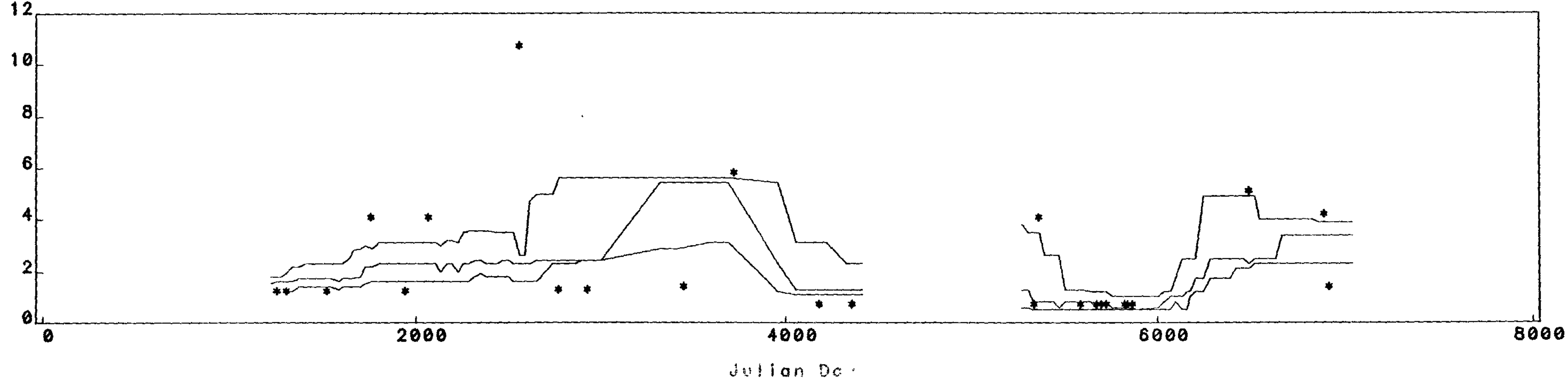
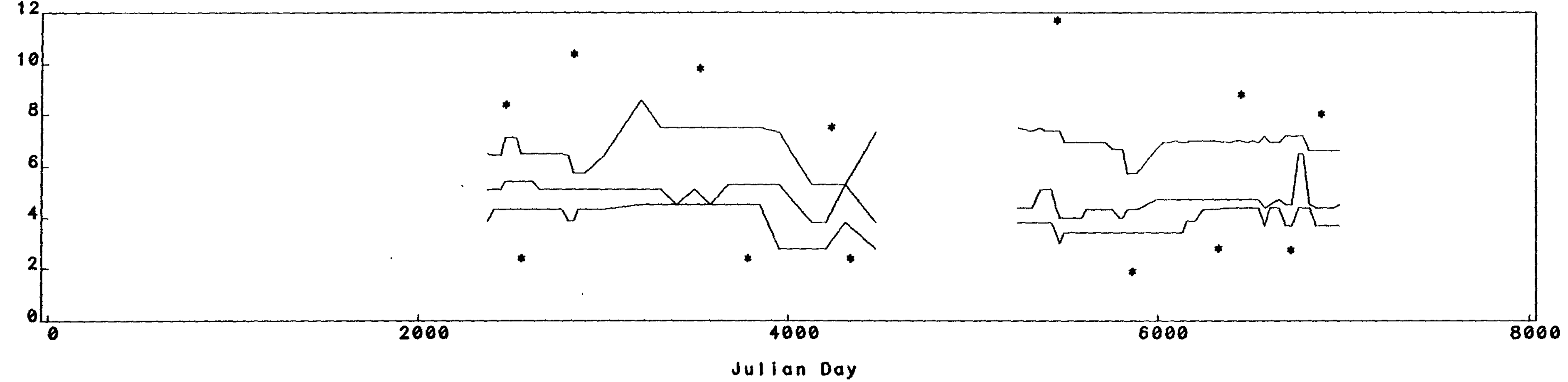

River no 3 Total Alkalinity

River no 4 Total Alkalinity



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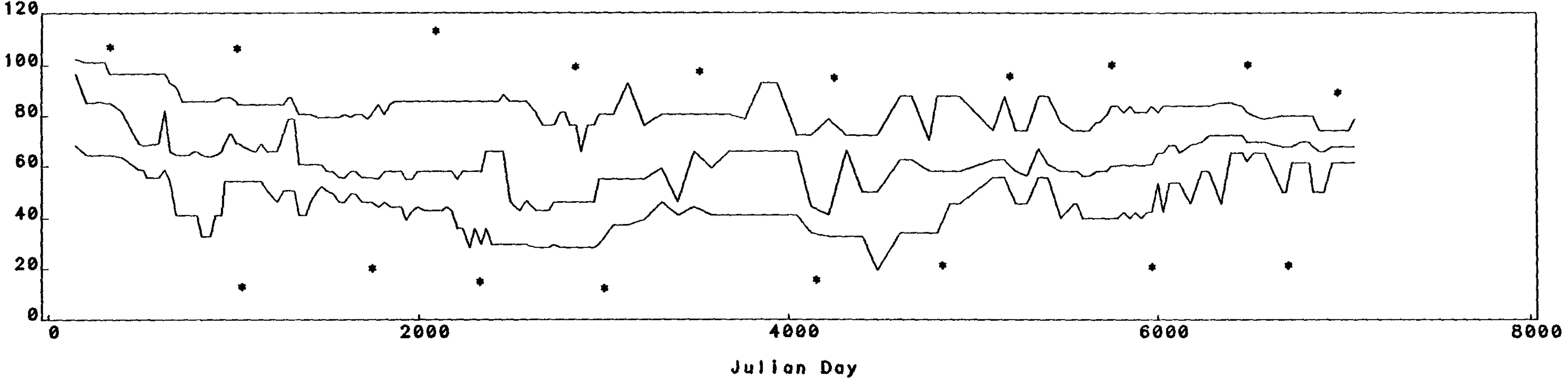

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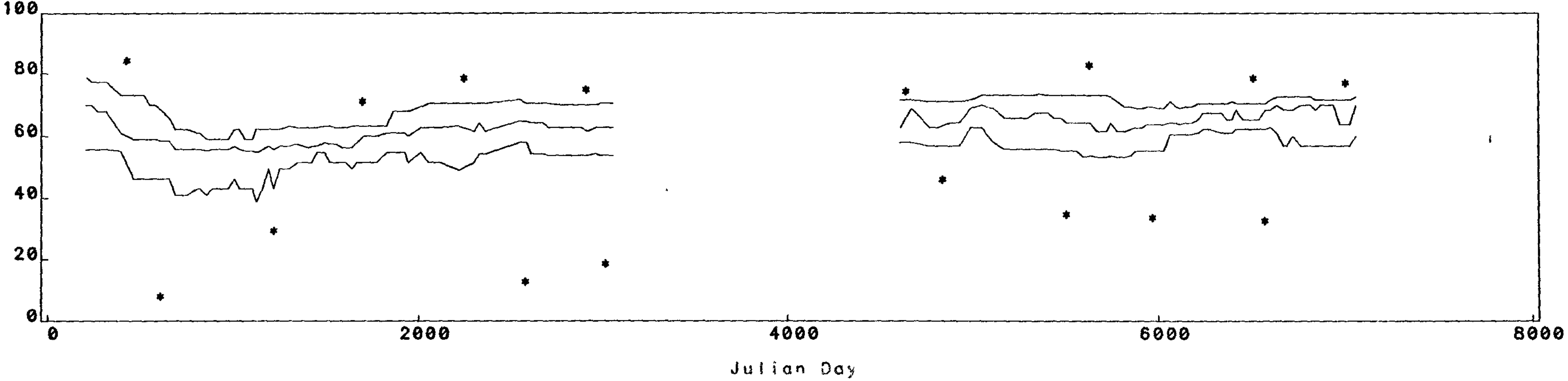

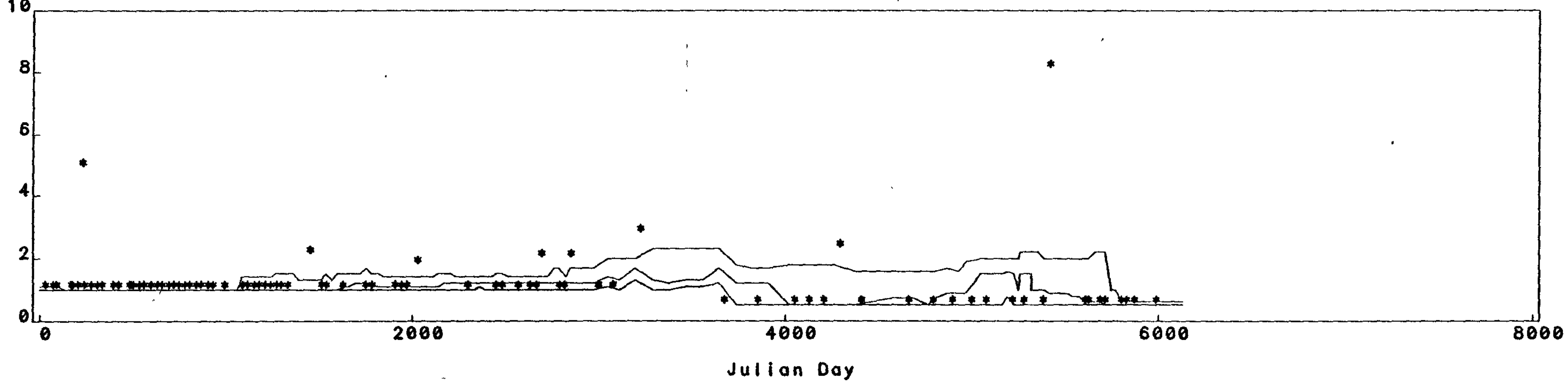
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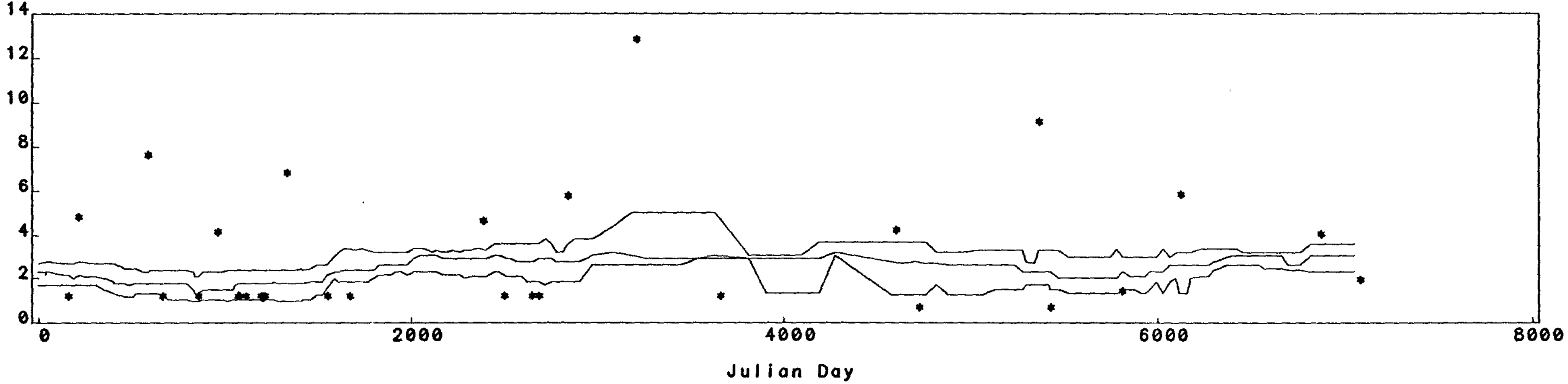
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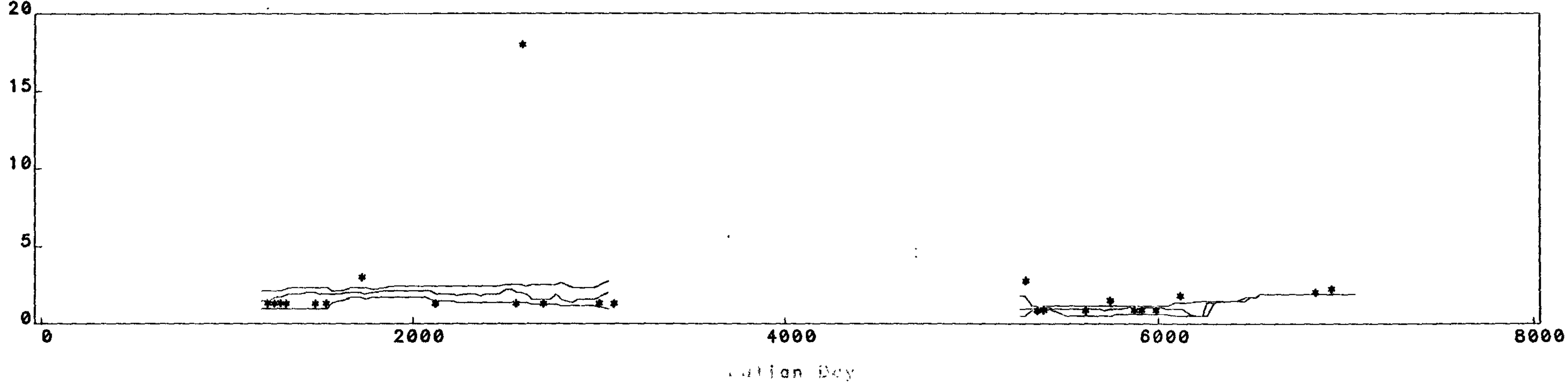
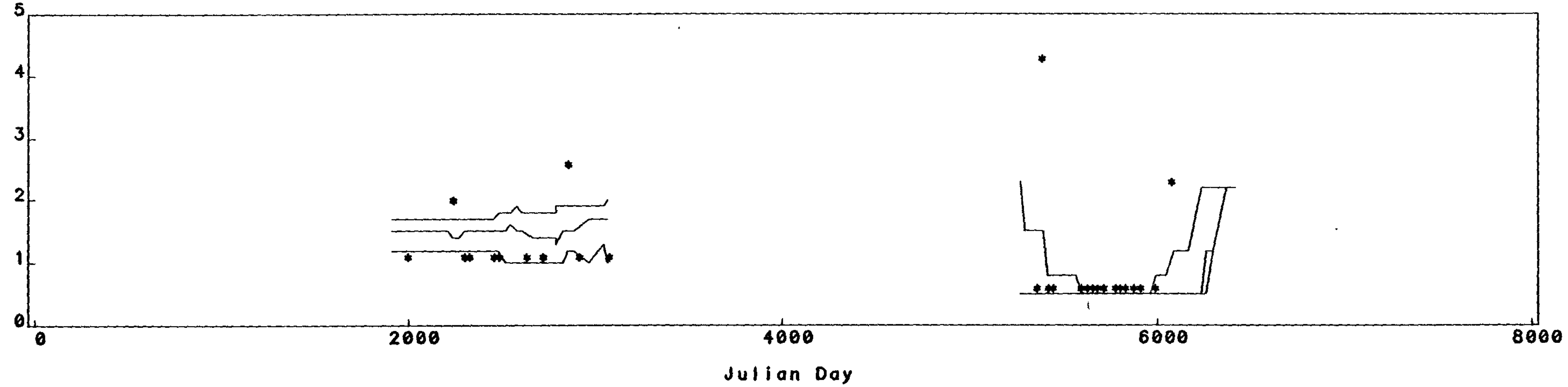
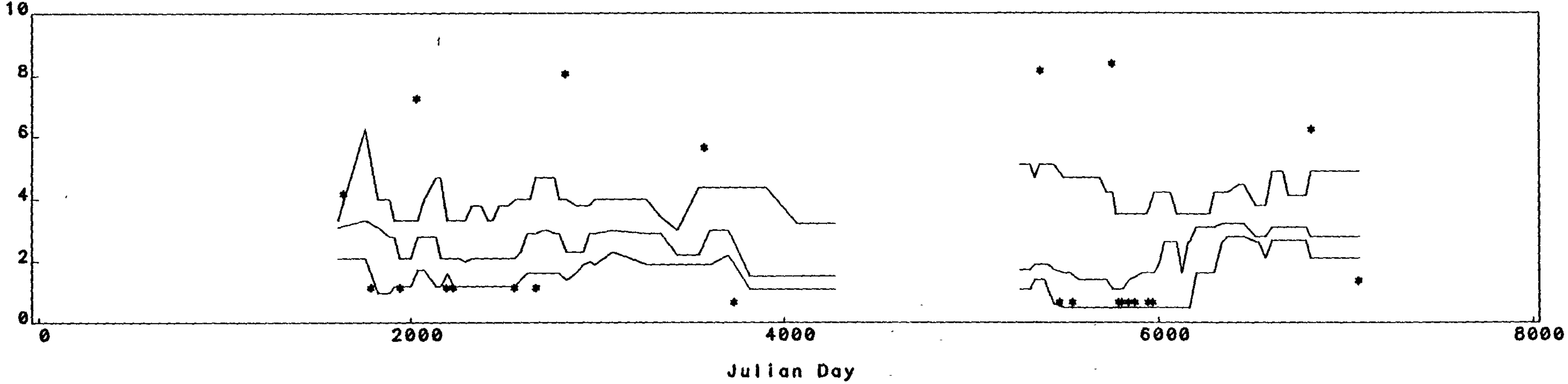

River no 9 Total Alkalinity

River no 10 Total Alkalinity



River no 11 Total Alkalinity



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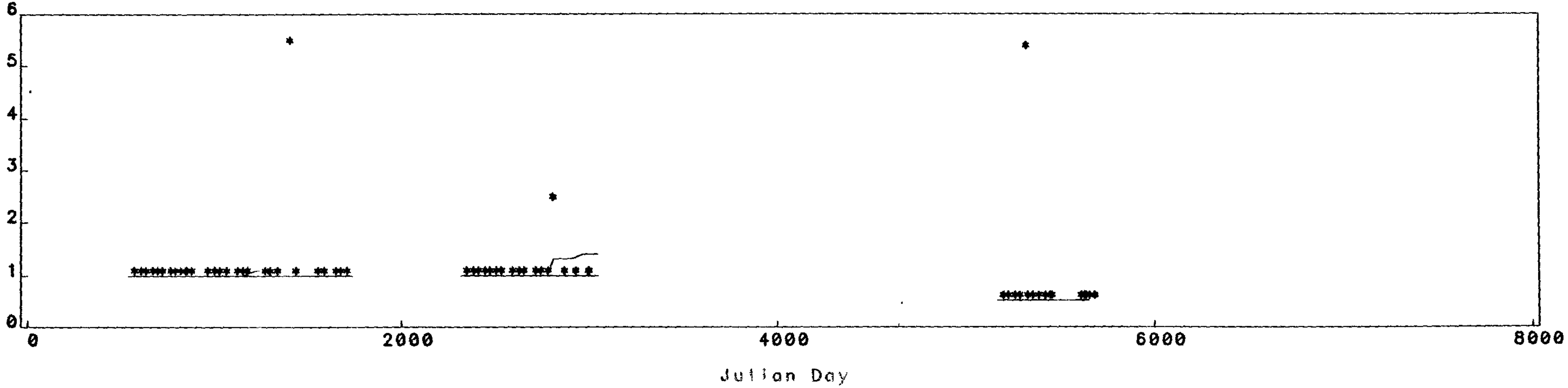

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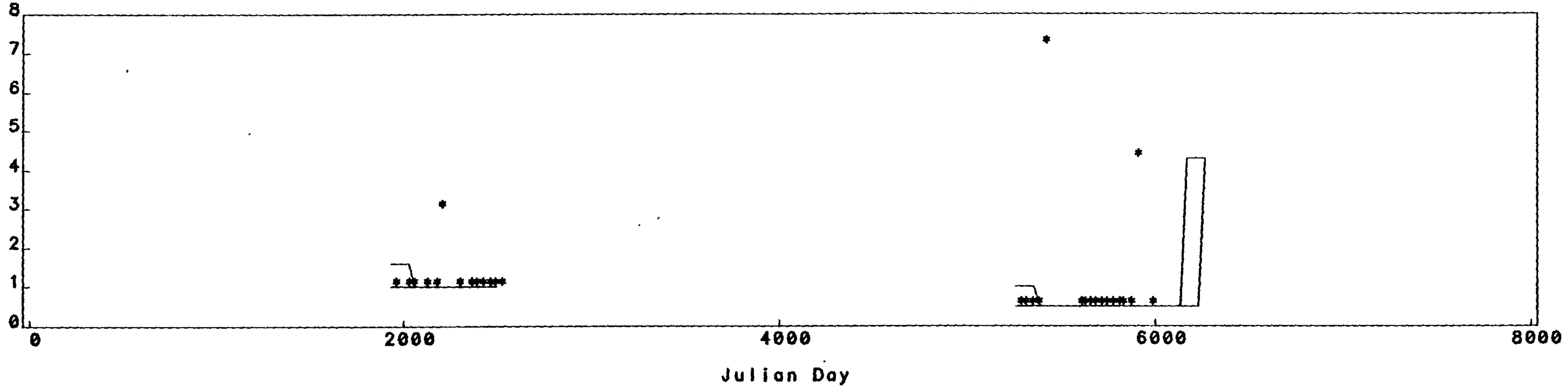

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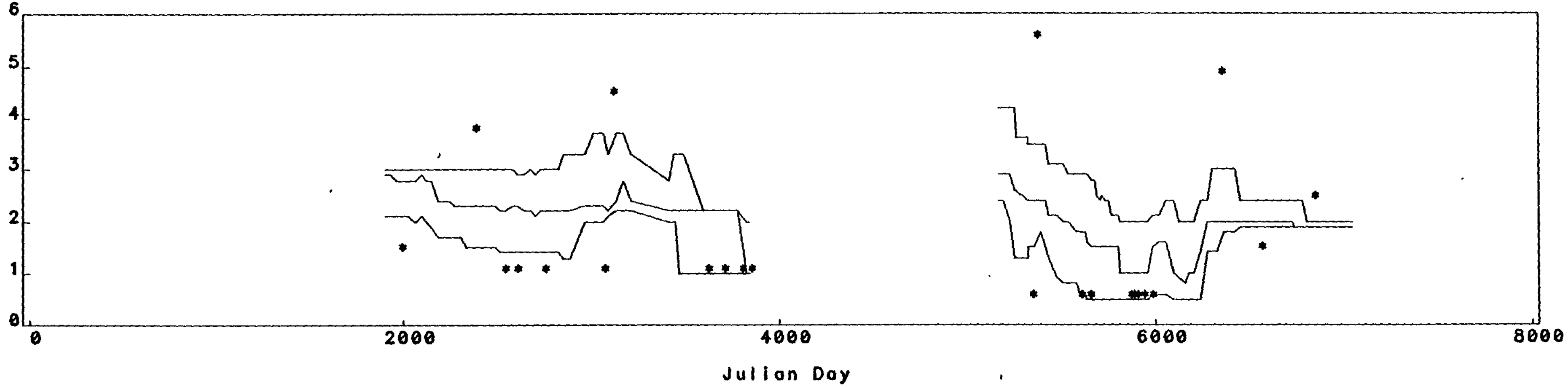

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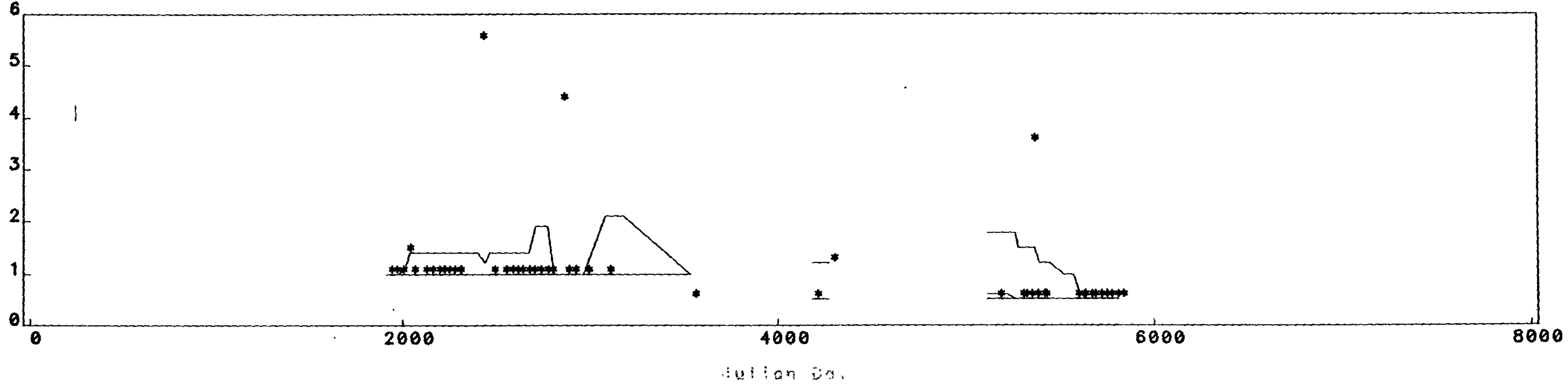

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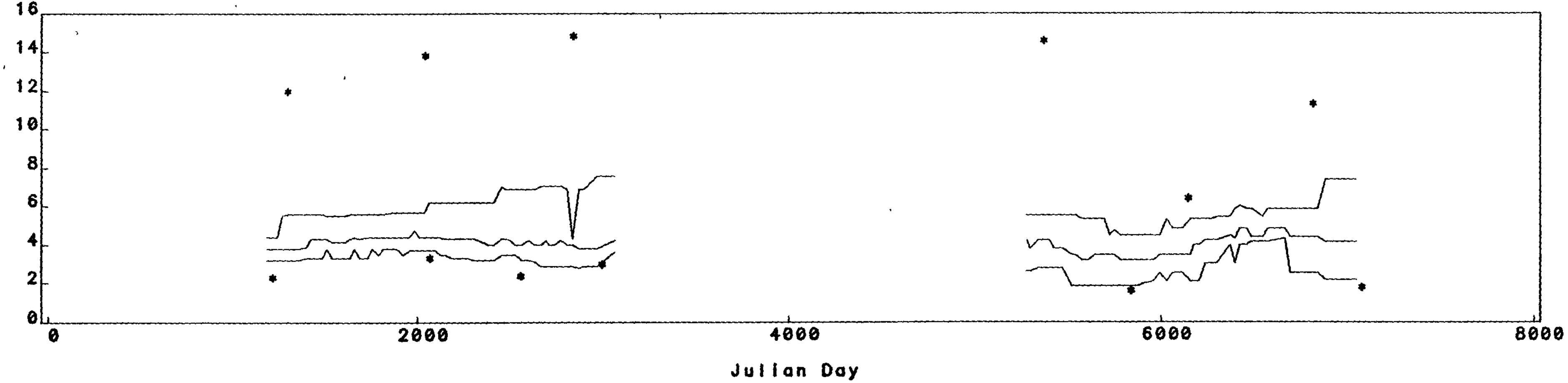

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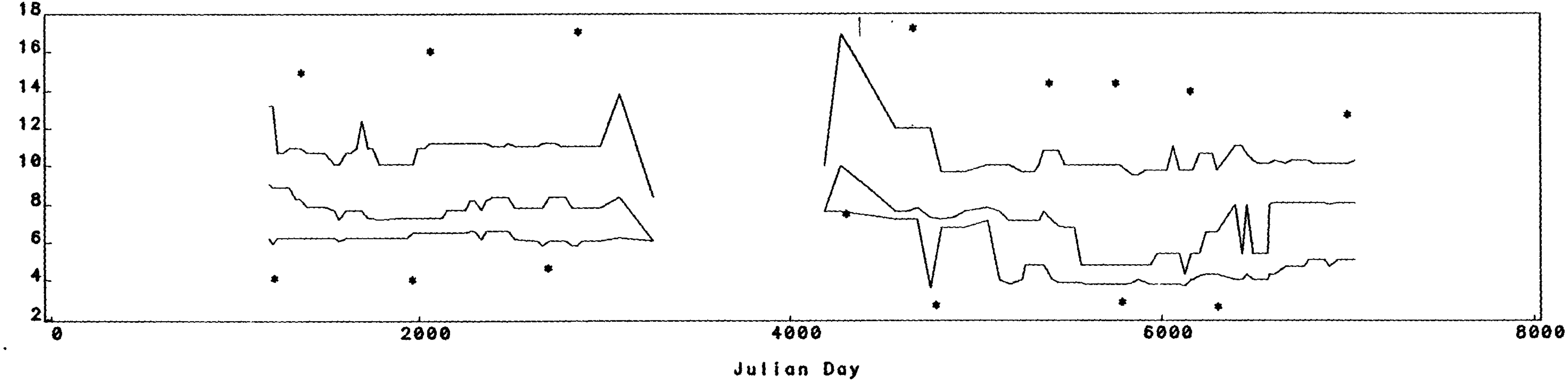

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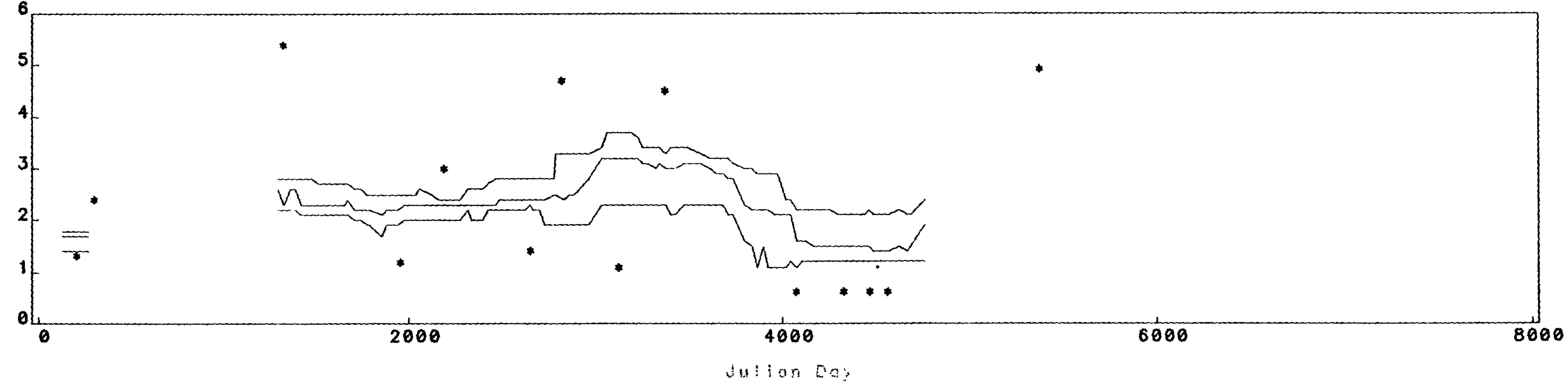
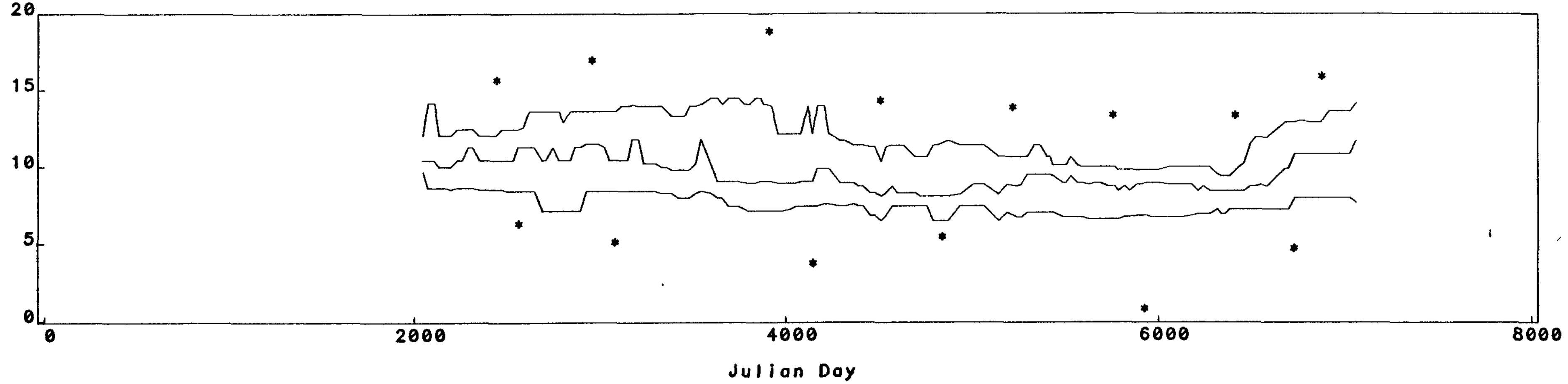


River no 21 Total Alkalinity



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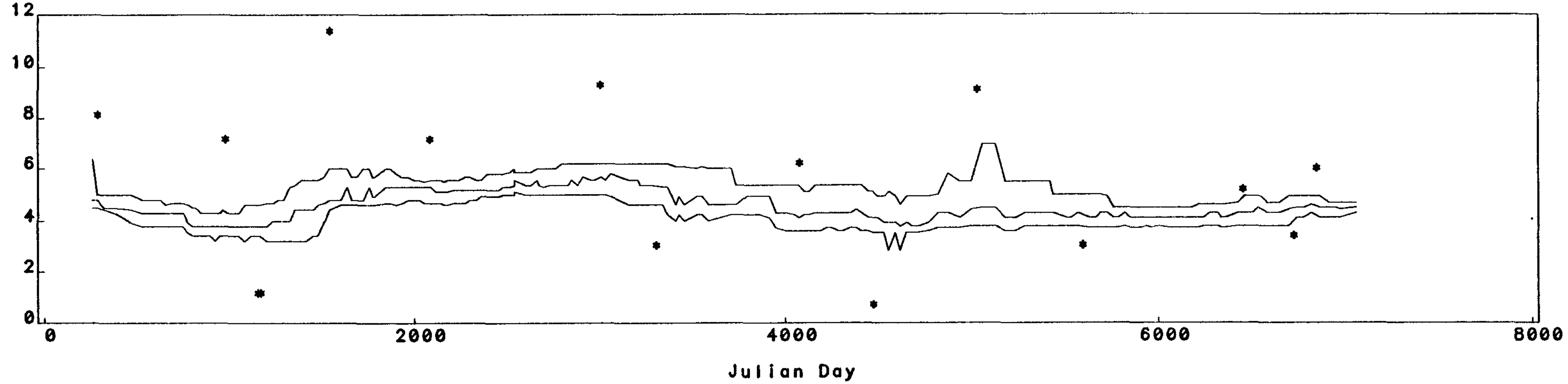
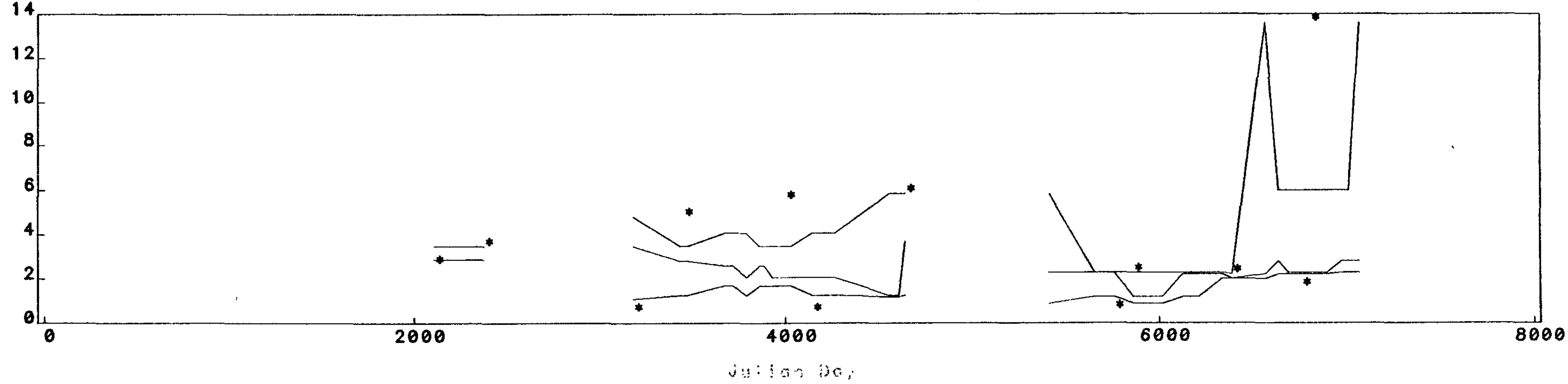


River no 23 Total Alkalinity



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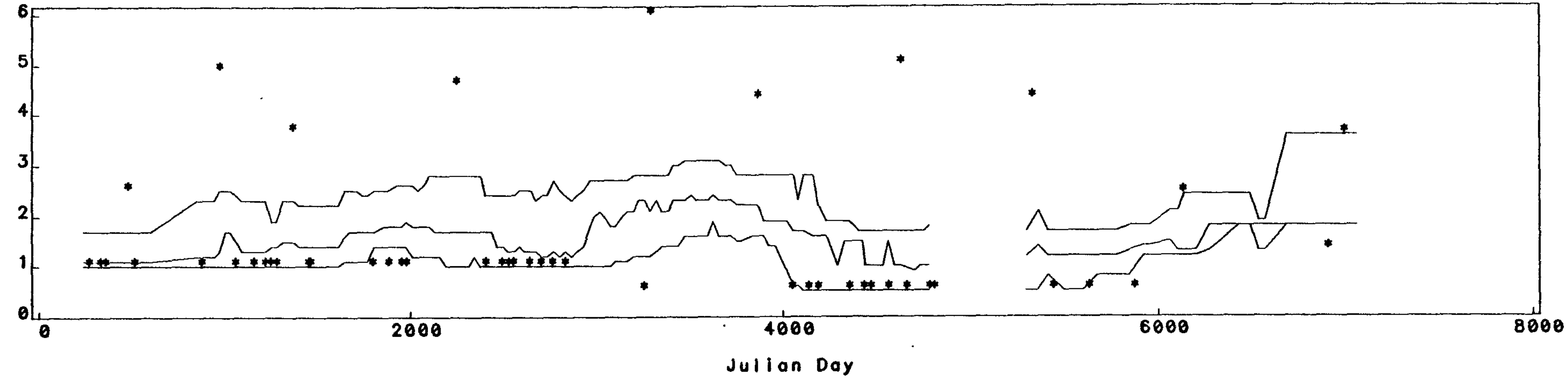
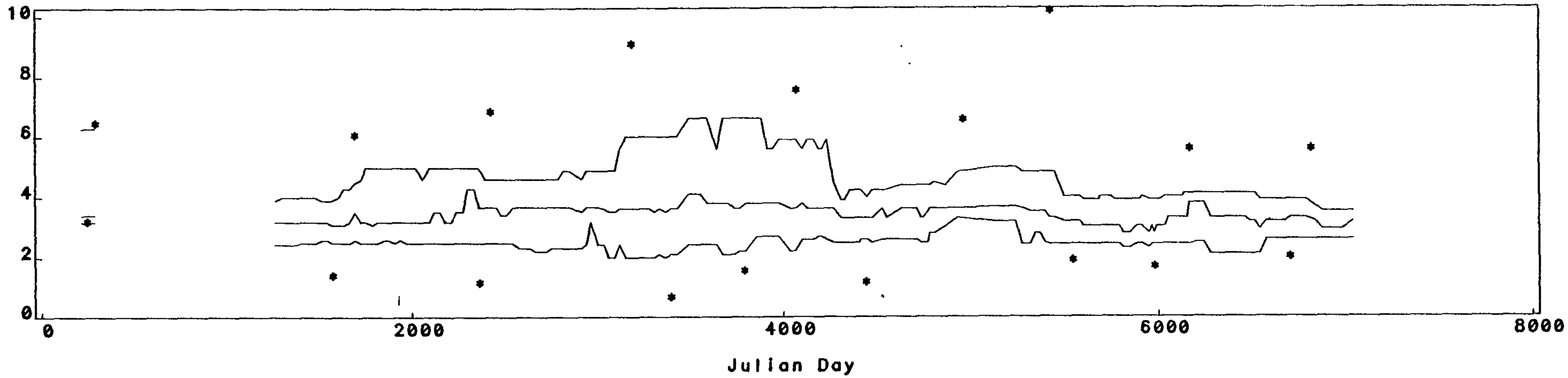
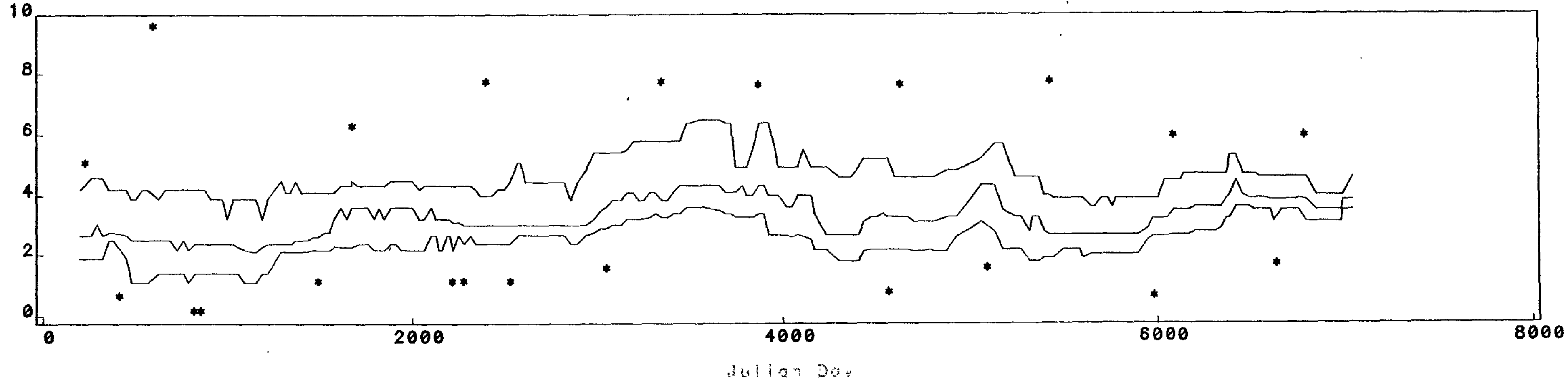
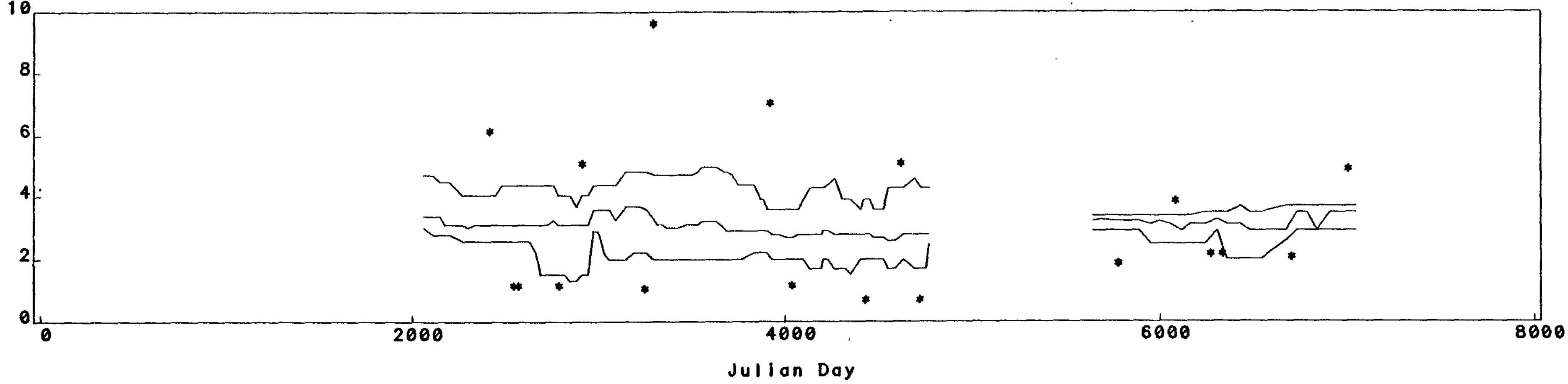


River no 26 Total Alkalinity



River no 27 Total Alkalinity

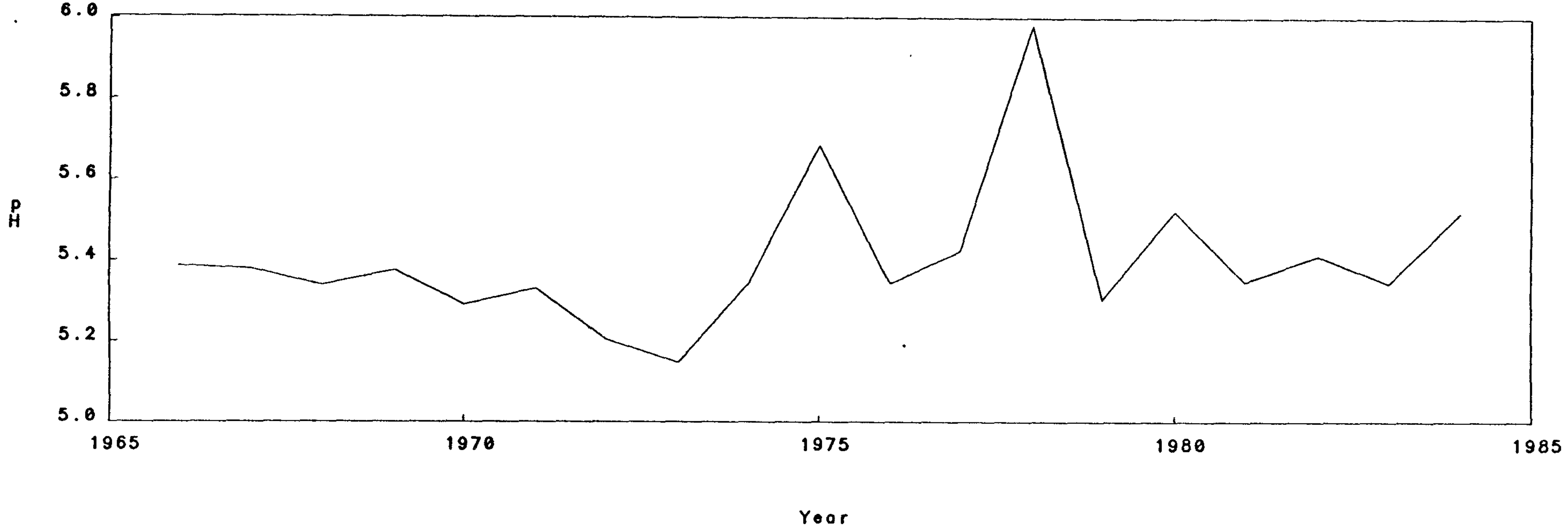




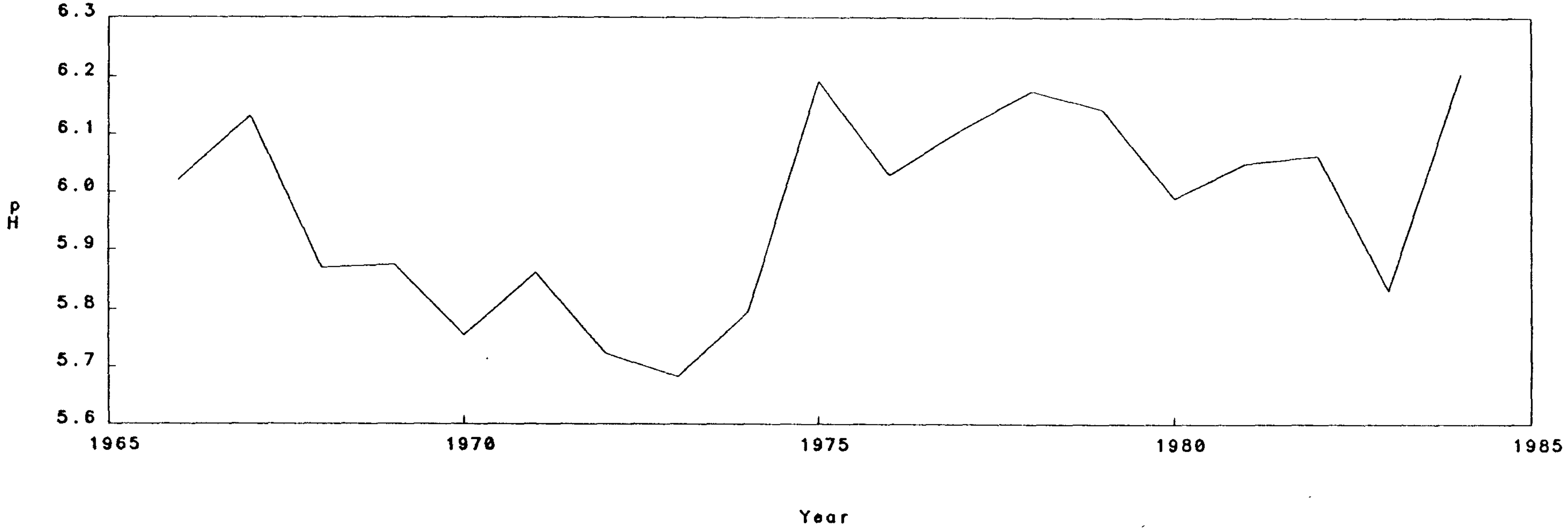
River no 28 Total Alkalinity

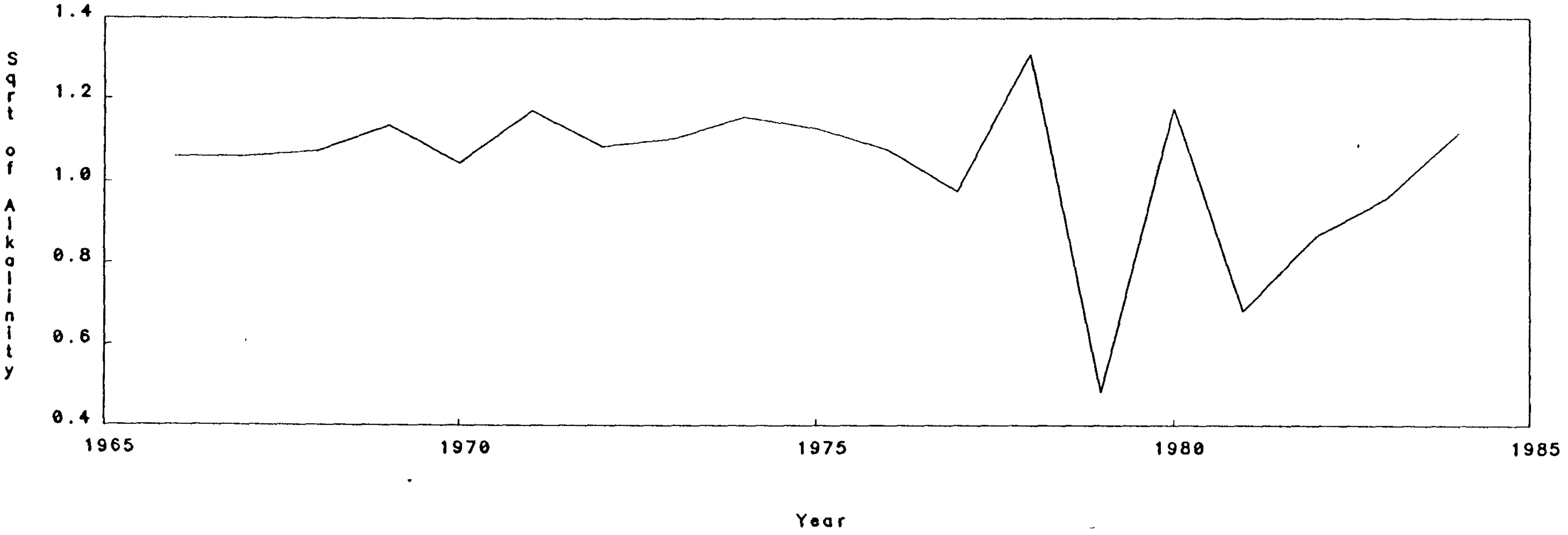
<u>Figure 13.</u> Plot of fitted year values from the ANOVA model of year effects, controlling for river effects.

Fitted yearly values of NS pH.

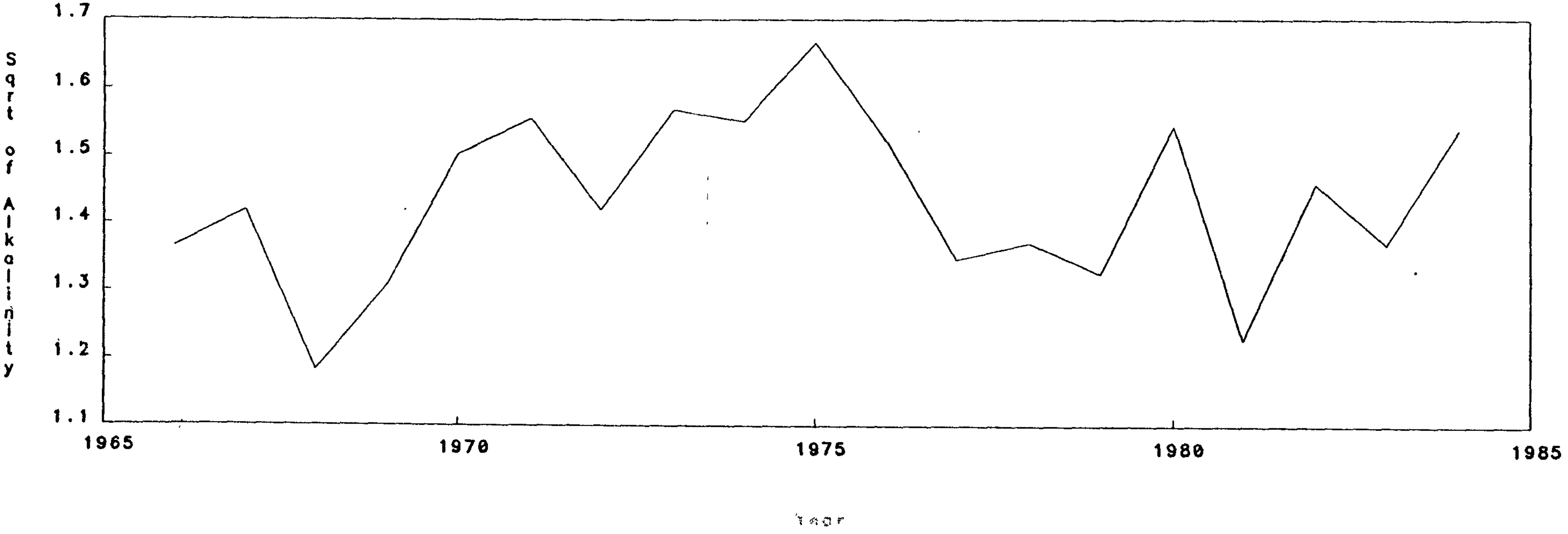


Fitted yearly values of Nfld pH.



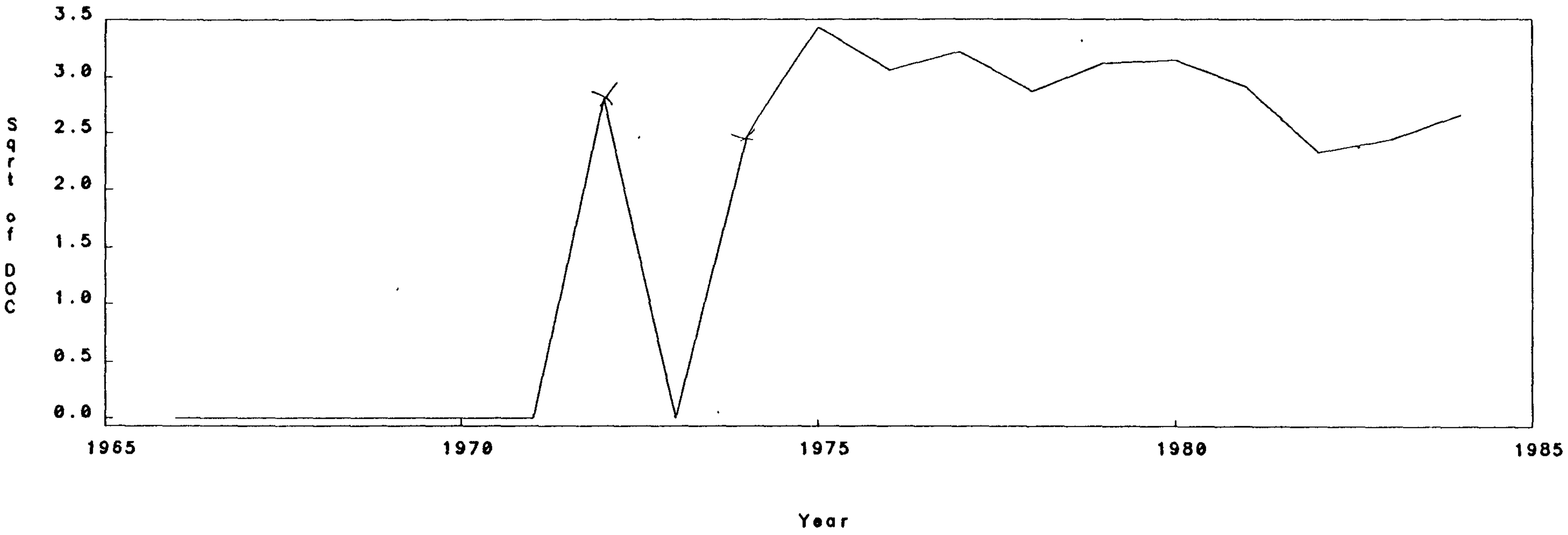


Fitted yearly values of NS Alk.

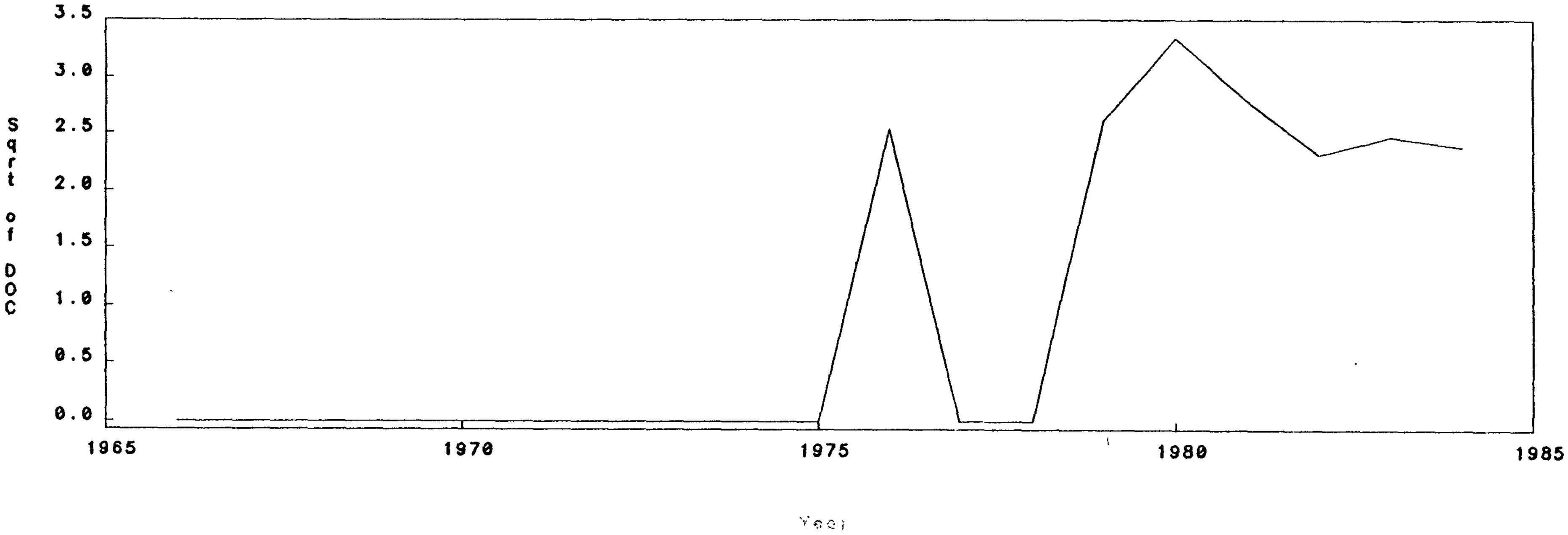


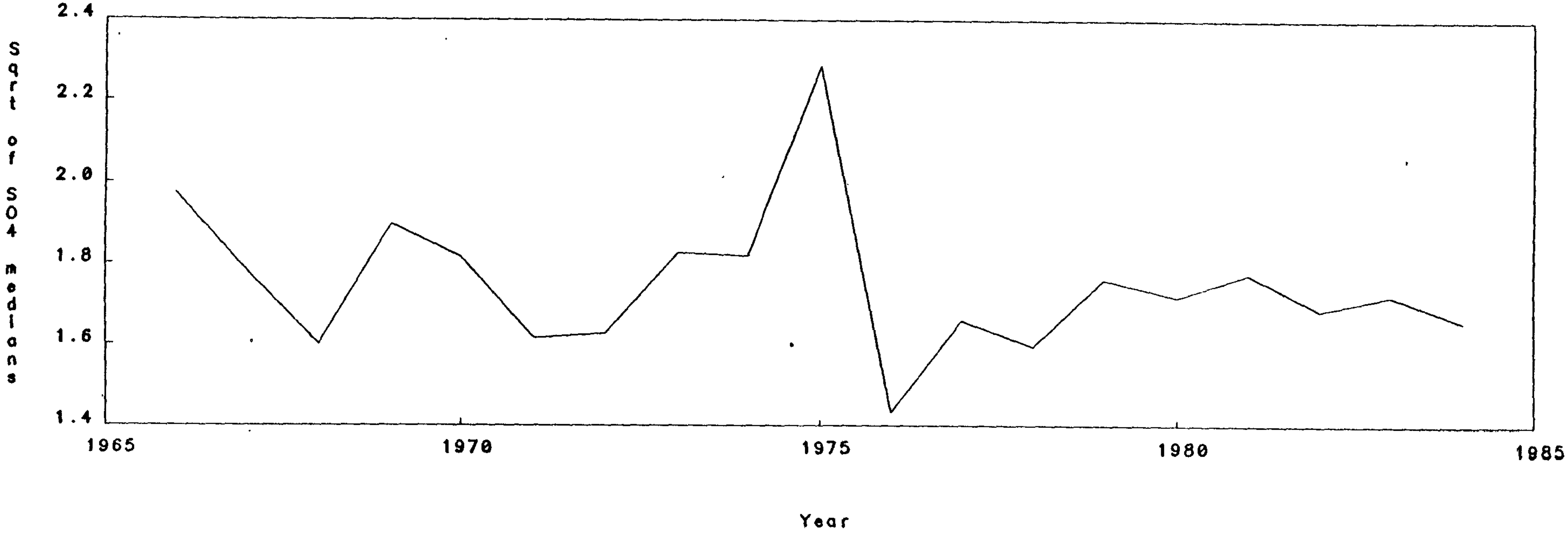
Fitted yearly values of Nfld Alk.

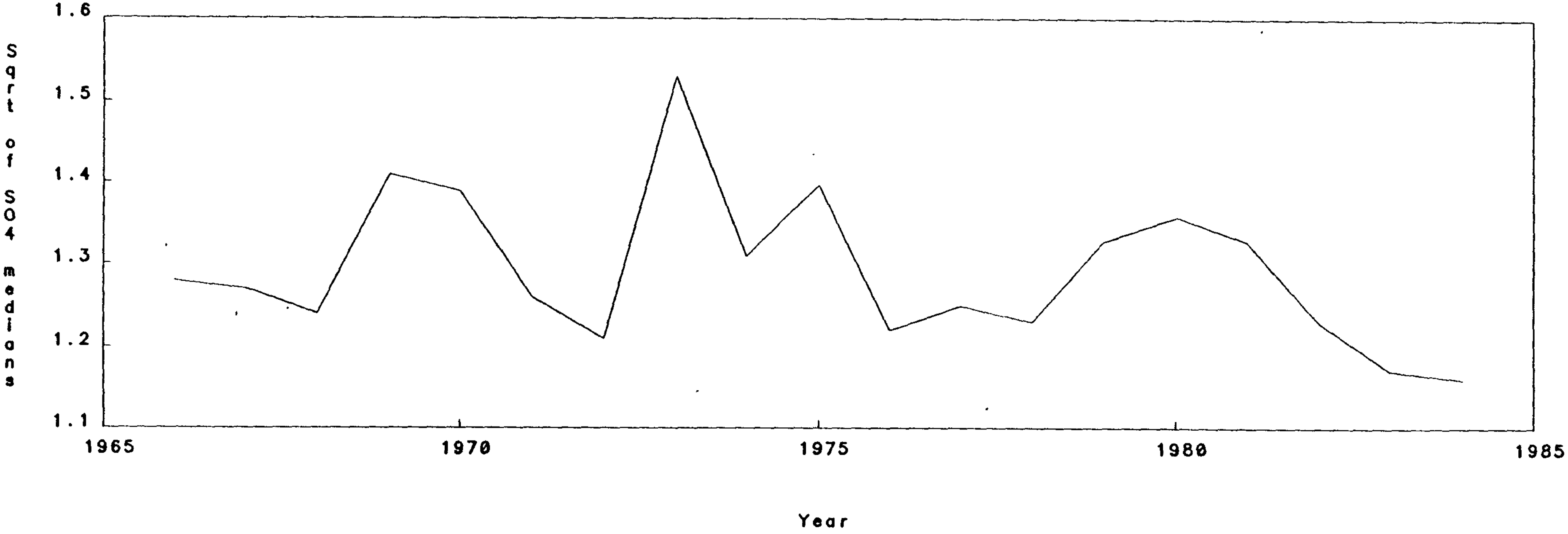
Fitted yearly values of NS DOC.

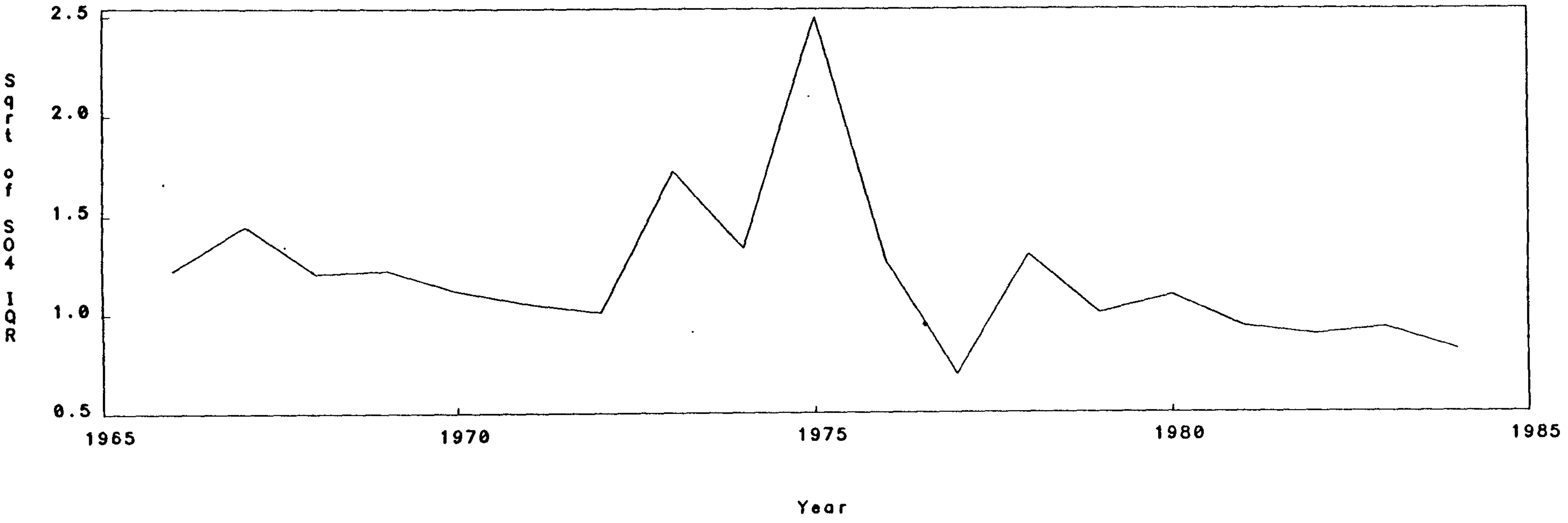


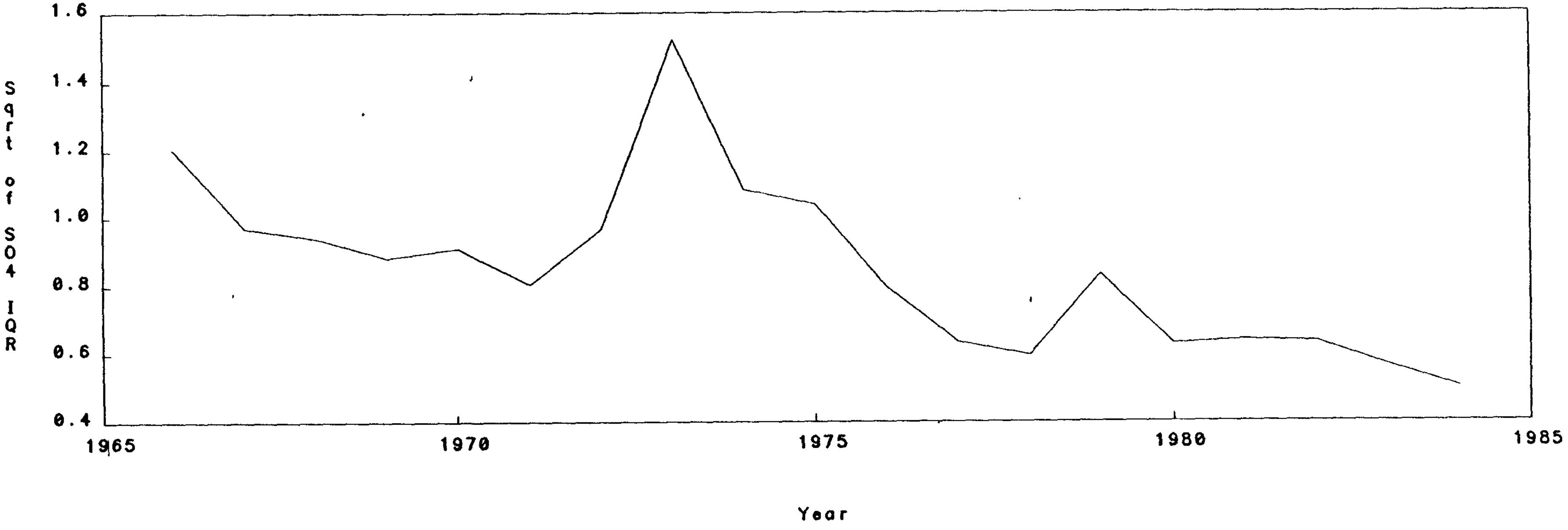
Fitted yearly values of Nfld DOC.




Fitted yearly values of NS SO4


Fitted yearly values of Nfld SO4


Fitted yearly values of NS SO4


Fitted yearly values of Nfld SO4