WORKING PAPER 478

# STATISTICAL MODELLING OF WATER COLOUR IN THE UPLANDS: THE UPPER NIDD CATCHMENT 1979-1985

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## INTRODUCTION

The uplands are a cheap source of potable water. Over the last decade, the quality of such waters has been deteriorating. This is especially noticeable in terms of the amount of colour. In some Pennine catchments, this has more than doubled in the last eight years. As a consequence, treatment costs have increased by as much as ten times at works where it is possible to remove the colour and, elsewhere, consumer complaints have shown similar increases. This has proved to be of great concern to water authorities such as Yorkshire Water which obtains about 50% of supply from Pennine catchments.

Increases in colour are also variously associated with increases in dissolved iron, aluminium and manganese. Whilst present levels of these elements are not such as to cause concern, it is important to begin to learn something of the mechanisms behind the deterioration in water quality. This is valuable both with respect to short term management strategies (McDonald and Naden, in press) and to long term planning and capital investment in new treatment works.

The upper Nidd catchment (figure 1) is one of the largest water-gathering grounds in Yorkshire and is a key element in the water supply system. As part of an intensive study, this paper presents an analysis of the discoloured water problem in this area for the period April 1979 to December 1985. It looks at the trends in water colour over time and, pertinent to the causes of increasing discoloration, investigates the relationships between colour, other water quality parameters and a number of rainfall-related variables.

## THE DATA

The work is based upon colour data provided by Yorkshire Water Authority. Measurements of colour and other water quality parameters, some of which are associated with changing levels of colour (e.g. pH, turbidity, conductivity and total aluminium, manganese and iron), are available for the raw waters arriving at Chellow Heights treatment works. Much of the water supplied to these works comes from Angram and Scar House reservoirs built early this century, and from a series of intakes in the How Stean catchment which were constructed in the 1960's to augment the supply (figure 1).

The colour measurements were made on samples of raw water filtered using 0.45 micron Millipore membrane filters. Colour is expressed in terms of absorbance per metre at a wavelength of 400 nanometres (HMSO, 1981; p.10). The frequency of measurements has varied considerably over the period from almost daily sampling to something less than weekly sampling.

Daily rainfall data for 1979-1985 measured at Scar House reservoir (grid reference SE065766) is also available and forms the basis for an analysis of the relationship between colour and the hydrological conditions on the catchment.

## LEVELS OF COLOUR

Table 1 gives the level of colour in the raw waters at Chellow Heights for the calendar years 1979 to 1985. The calendar year was chosen in preference to the water year because there is usually a marked increase in colour in the autumn which sometimes, but not always, straddles the division between water years.

Values of mean annual colour have varied from 4.33 $ab.m^{-1}$ in 1984 to 6.65 $ab.m^{-1}$ in 1985. The apparent change in the variance of the colour measurements is partly an artefact of the changing sample size although there has been a tendency towards more extreme values.

Comparing the data for each year, there are significant variations ($F=17.68$; $df=7,1094$; $p<0.001$) from year to year. These are largely due to two significant (based on Duncan's New Multiple Range Test - Kramer, 1956) jumps in colour during the period of record. The first was in 1981 after which colour returned to its former level and the second was in 1985. It is yet to be seen if this second jump in colour is to be reversed.

Looking in more detail at the pattern of colour through time, figure 2 reveals a general increase in colour superimposed upon a marked seasonal variation with peak colour levels in the autumn. Taking 1st January 1979 as day 1, the upward trend in colour can be expressed as the linear relationship

$$\text{COLOUR} = 4.37 + 0.000575 \text{ DAY}$$

This is a statistically significant trend at the 0.001 confidence level ($n=1102$) but it only accounts for 3.6% of the variation in colour.

To examine the seasonal variation in the data, it is necessary to remove the linear trend and look at the pattern in the residuals. An analysis of the autocorrelation between the residuals reveals two scales of dependence (Richards, 1979) - the first, a strong 3-monthly positive dependence (significant at 99.5% level) between the data points and the second, a weaker (significant at 89% level) annual pattern.

Another way of looking at the residuals from the linear trend is to identify the peaks in the data, particularly what might be described as the autumn flush of colour. Colour peaks may be said to begin when colour rises above one standard deviation away from the mean and to continue until colour consistently falls below this level (i.e. values above the dashed line in figure 2). It is, therefore, not necessarily a continuous peak but a period during which high colour flows occur. Table 2 shows the date of the onset and duration of these key periods. Dates are approximate in so far as they are highly dependent on the frequency of sampling. Individual high spots (identified from single samples) which occurred in summer 1981, spring 1983 and July 1984 have been omitted.

The onset of the period of enhanced colour is usually September or October except in exceptionally wet summers such as that of 1980 when the autumn flush began in July. There is much more consistency in the timing of the cessation of enhanced colour flows which may be related to temperature or snowfall on the catchment. With the exception of 1983, the autumn flush lasts for about three months on average although it can last up to 5 or 6 months in years with wetter than average summers such as 1980 and 1985. The absence of a marked autumn flush in 1983 following a peak in colour in April and May of that year perhaps raises questions as to the size of the colour store on the catchment.

## POSSIBLE CAUSES OF DISCOLORATION

There are a number of possible causes for the recent increase in the discoloration of runoff. These can be divided into three categories - increasing rainfall acidity, land use changes and climatic variability.

Changes in atmospheric chemistry since 1750 have affected the uplands (Binns and Redfern, 1983). Episodes of acid rainfall may increase the mobility of a number of elements, such as iron, manganese (Neal *et al.*, 1986) and aluminium (Bache, 1986), which are often associated with discoloration. Reduction in the amount of *Sphagnum* moss has led to increased erosion on catchments (Phillips *et al.*, 1981) both by wind and by headwater extension of tributary streams. This may increase colour levels by increasing the amount of peat particulates in runoff from which colour may be derived or by exposing areas of peat on the surface of the catchment to drying out processes. This might be especially important if the lower horizons of the peat, having a higher degree of humification, are tapped.

Land use changes have also seriously affected the uplands. Increases in stocking levels of sheep and grouse have led to increases in erosion. Over the last two decades, decreases in grants for liming have meant that the total lime applied in England and Wales has been halved. Again, this has the effect of increasing acidity and, therefore, mobilising elements in the peat or releasing those in stream sediment storage. Other land use changes such as moorland gripping and less-controlled burning of heather areas result in the exposure of peat to decomposition and erosion. The relevance of each of these factors will vary greatly both between and within catchments (McDonald and Naden, in press). Evidence for the effectiveness of such mechanisms for releasing colour could suggest ways of reducing the discoloration of runoff by changing land management practices rather than increased investment at the treatment works.

The association of colour changes with the drought years of 1976 and 1984 also suggest that the lowering of the water table to a greater depth than normal may lead to an increase in colour due to the aerobic decomposition of the organic layers in upland soils.

## Relationships between colour and other water quality parameters

In assessing the possible causes of discolouration, a simple first step is to look at the association of colour with other water quality parameters. For example, changes in pH may suggest the importance of episodes of acid rainfall; turbidity may indicate the association of colour with erosion and the release of particulates; conductivity may indicate changes in the catchment chemistry; aluminium, manganese and iron might help to define the chemical compounds associated with the colour. One drawback of the database being used is that the water is sampled at the water treatment works some 50 km from the colour sources and after varying reservoir storage times. The extent of water quality changes between the catchment and the treatment works are as yet unknown, as are the effects of storage time. As a result, the relationships investigated below are indirect, and sensitive indicators, such as pH in particular, may bear little relation to what is happening on the catchment.

Table 3 summarises the data for pH, turbidity, conductivity, total aluminium, total iron and total manganese for the years 1979 to 1985. Also indicated are any trends in these water quality parameters with time and any association with colour levels. Over time there have been significant increases in pH, turbidity, aluminium, manganese and iron as well as colour with the most significant increases being in turbidity, aluminium and iron. Colour appears to be positively associated with turbidity, aluminium, manganese and iron while pH and conductivity show a negative relationship with colour. The significance of both these sets of relationships is to a certain extent due to the large sample sizes. However, they do suggest that some chemical changes, either natural or man-made, have taken place on the catchment and that colour, in addition to having a dissolved or throughflow component, may also be associated with erosion and the transport of peat particulates. However, in assessing the mechanisms of release from soil water sources, relationships between colour and rainfall may also be valuable source of information.

Relationships between colour and rainfall-related parameters

There is no relationship between colour and daily rainfall. This is to be expected in so far as there are several different time lags built into the hydrological processes delivering water to the reservoirs and intakes, and a second set of time lags built into the reservoir storage and delivery of water to the treatment works. Without specifying the order of magnitude of such lags, it is impossible to account for the day to day variations in colour. However, by looking at the average monthly colour levels and monthly rainfall (figure 3), it may be possible to get some idea of the dependencies within the system.

Short term measurements of colour variations on the catchment have indicated the importance of a 'washing out' process as colour increases over an individual hydrograph event. The importance of this process should be reflected in the correlation between total monthly rainfall and average colour levels for the month. Figure 4 shows the increase in colour levels with increasing monthly rainfall and this relationship explains 15.1% of the variation in colour levels. It is interesting to note, however, that colour levels for September and October 1985 are significant outliers from this relationship. This implies that the sudden jump in colour in 1985 is not simply a result of higher rainfalls washing out more of the colour stored on the catchment.

It has been suggested, based on the evidence from colour levels in 1976-1978 (Haworth, pers. com.), that sudden jumps in colour have followed extremely dry summers and, therefore, some measure of the moisture deficit is required. Consequently, the monthly rainfall amounts were cumulated, a regression line fitted and the residuals from that line taken to indicate roughly the moisture variations (figure 5). The technique is analogous to the single mass curve used in the analysis of long-term water yield. Negative values indicate high moisture deficits; positive values show wetter than average moisture values.

A cross-correlation between mean monthly colour values and this index of moisture excess or deficit indicates that the two are significantly negatively related at lags of 3 and 14 months. In other words, autumn colour is high following a dry summer and a dry previous summer. This is in line with the suggestion that the colour store of the catchment is increased during droughts and is subsequently slowly removed, but it may also relate to the length of time over which water is stored on the catchment. Figures 6 and 7 show the relationships between colour and 3-month and 14-month previous moisture indices - MI3 and MI14 - respectively. Individually, they explain 33.8% and 27.0% respectively of the variance in the colour data.

With respect to the long-term trend in colour levels and the jump in colour in 1985, it is also of interest to look at the pattern of the moisture index over the period. Figure 8 shows that in the run-up to the 1984 drought, moisture levels had been steadily increasing whereas since then, despite the wet summer of 1985, the moisture index is still below the average for the period.

Putting the three rainfall associated variables together, it is clear that they are not independent of each other as shown by the correlation matrix below.

| | RAIN | MI3 | MI14 |
|---|---|---|---|
| COLOUR | 0.389 | -0.581 | -0.520 |
| RAIN | - | -0.368 | -0.263 |
| MI3 | - | - | 0.391 |

(Underlining indicates significant correlation coefficients at 0.001 level)

However, despite the fact that the correlations between the rainfall and moisture indices are statistically significant, they are not large enough to be of practical concern (Chatfield & Collins, 1980). Consequently, a stepwise regression analysis of colour versus current monthly rainfall, 3-month previous moisture index and 14-month previous moisture index was performed and gives the following equation:

$$\text{COLOUR} = 5.19 - 0.00588\ \text{MI3} - 0.00355\ \text{MI14} + 0.00173\ \text{RAIN}$$

$$(n = 68;\ r = 0.718;\ p<0.001)$$

Just over 51% of the variance in mean monthly colour levels is explained by this combined rainfall and moisture index model. High soil moisture deficits are associated with negative values of MI3 and MI14 and, therefore, add to the available colour while high rainfall in the current month promotes high colour through the washing out process. In terms of explanation, 43% of the monthly colour variance is explained by the moisture index 3 months previous; 8.2% by the moisture index 14 months previous and just 0.005% by the current month's rainfall. The low level of explanation provided by the current month's rainfall suggests that the effect of the washing out process, observed over a hydrograph, is blurred by taking monthly figures and by the series of time lags between flows on the catchment and the arrival of water in the treatment works. This variable might then be removed from the analysis. The most important control on the monthly colour levels at the treatment works is instead the variation in the colour store on the catchment as related to longer term changes in moisture levels.

## CONCLUSION

Although marked seasonal and year on year variations are apparent, a significant upward trend in discoloration is identified. The time of onset of the autumn colour peak is quite variable. However, the time of cessation of this colour flush is fairly constant over the period of record. Colour is positively related to monthly rainfall but the highest colour values remain as outliers from this relationship. Colour is therefore not simply related to rainfall totals during the colour peak. The analysis of moisture deficit prior to the time of sampling indicates that moisture deficit three months and fourteen months prior to the time of sampling explain more than 50% of the variations in colour.

Colour is positively related to aluminium, iron, manganese and turbidity. Colour is negatively related to pH and conductivity. The negative conductivity and the positive turbidity relationships suggest that the colour phenomenon is not solely a chemical relationship but that an erosional component might be involved.

This analysis identifies the significance, to the autumn colour flush, of drought conditions on the catchments in the previous two summers. In an earlier paper (McDonald and Naden, in press), the authors indicated that drained catchments appear to yield more colour. This would correspond to the drought mechanism identified from the work reported here. These results suggest the need for more direct measures of moisture deficit to be related to colour monitoring on the catchments.

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## ACKNOWLEDGEMENTS

We should like to thank Yorkshire Water Authority for the use of their data and the University of Leeds Research Fund for financial support.

TABLE 1 Colour levels in the raw waters at Chellow Heights (1979-1985)

| YEAR | NO.SAMPLES | MEAN COLOUR ($ab.m^{-1}$) | ST.DEV. ($ab.m^{-1}$) | MAX.COLOUR ($ab.m^{-1}$) |
|---|---|---|---|---|
| 1979* | 77 | 4.83 | 1.35 | 7.70 |
| 1980 | 337 | 4.68 | 1.77 | 9.65 |
| 1981 | 343 | 5.29 | 0.89 | 8.30 |
| 1982 | 177 | 4.54 | 1.47 | 9.50 |
| 1983 | 70 | 4.58 | 1.38 | 10.50 |
| 1984 | 50 | 4.33 | 2.45 | 13.00 |
| 1985 | 46 | 6.65 | 2.20 | 11.80 |

* from April

TABLE 2 Timing and duration of Autumn flush 1979-1985

| YEAR | ONSET | END | DURATION (days) |
|---|---|---|---|
| 1979 | 4.09.79 | 10.12.79 | 97 |
| 1980 | 1.07.80 | 15.12.80 | 167 |
| 1981 | 2.10.81 | 5.01.82 | 95 |
| 1982 | 14.10.82 | 9.12.82 | 56 |
| 1983 | an autumn rise but not a marked peak | | |
| 1984 | 11.10.84 | 9.01.85 | 72 |
| 1985 | 6.09.85 | 7.03.86 | 183 |

TABLE 3 Other water quality parameters and colour

a. Water quality levels

| | 1979* | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 |
|---|---|---|---|---|---|---|---|
| colour ab.$m^{-1}$ | 4.83 | 4.68 | 5.29 | 4.54 | 4.58 | 4.33 | 6.65 |
| pH | 6.14 | 6.44 | 6.56 | 6.53 | 6.55 | 6.55 | 6.53 |
| turbidity ftu | 4.99 | 6.78 | 5.27 | 10.33 | 7.14 | 10.32 | 11.50 |
| conductivity ms.$cm^{-1}$ | 73.9 | 69.3 | 71.5 | 84.2 | 74.0 | 88.2 | 81.2 |
| aluminium mg.$l^{-1}$ | 0.13 | 0.17 | 0.15 | 0.15 | 0.12 | 0.27 | 0.35 |
| iron mg.$l^{-1}$ | 0.55 | 0.70 | 0.68 | 0.69 | 0.59 | 1.10 | 1.13 |
| manganese mg.$l^{-1}$ | 0.05 | 0.07 | 0.04 | 0.07 | 0.06 | 0.23 | 0.22 |

* from April

b. Trends in water quality over time

| | Regression equation | $R^2$ | n | sig.level |
|---|---|---|---|---|
| colour | 4.37 + 0.000575 Day | 0.036 | 1102 | 0.001 |
| pH | 6.29 + 0.000151 Day | 0.046 | 517 | 0.001 |
| turbidity | 4.79 + 0.00275 Day | 0.061 | 744 | 0.001 |
| conductivity | 69.1 + 0.00613 Day | 0.024 | 287 | 0.01 |
| aluminium | 0.077+ 0.000087 Day | 0.179 | 284 | 0.001 |
| iron | 0.44 + 0.000263 Day | 0.126 | 313 | 0.001 |
| manganese | −0.016+ 0.000093 Day | 0.059 | 313 | 0.001 |

c. Relationships between colour and other water quality parameters

| | Regression equation | $R^2$ | n | sig.level |
|---|---|---|---|---|
| pH | colour = 10.1 − 0.810 pH | 0.048 | 515 | 0.001 |
| turbidity | colour = 4.45 + 0.054 turb | 0.045 | 742 | 0.001 |
| conductivity | colour = 6.01 − 0.0125 cond | 0.035 | 285 | 0.002 |
| aluminium | colour = 4.13 + 4.41 Al | 0.112 | 282 | 0.001 |
| iron | colour = 4.11 + 0.985 Fe | 0.07 | 312 | 0.001 |
| manganese | colour = 4.75 + 1.25 Mn | 0.01 | 312 | 0.002 |

## List of Figures

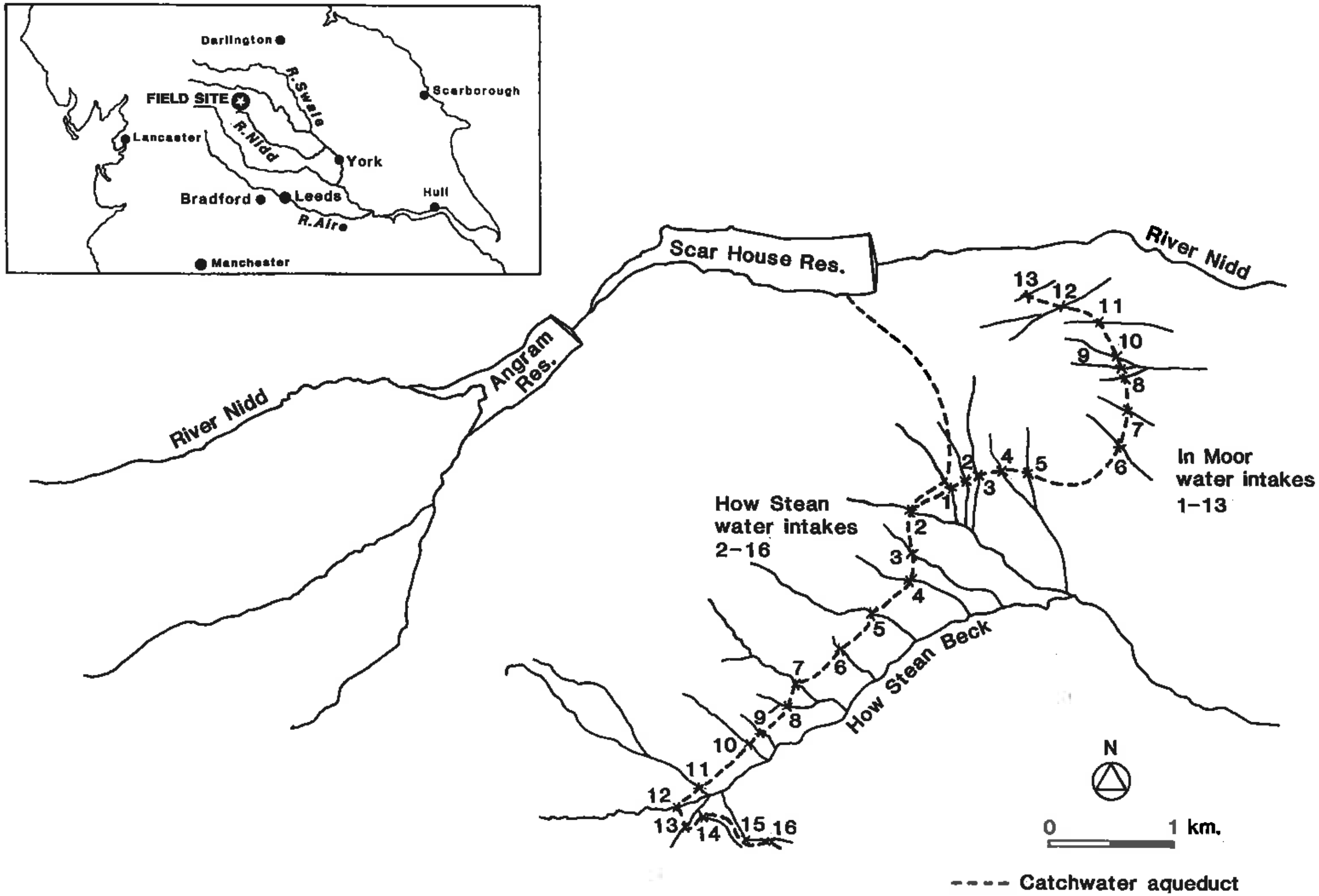


Figure 1 Upper Nidd catchments showing How Stean and In Moor intake system

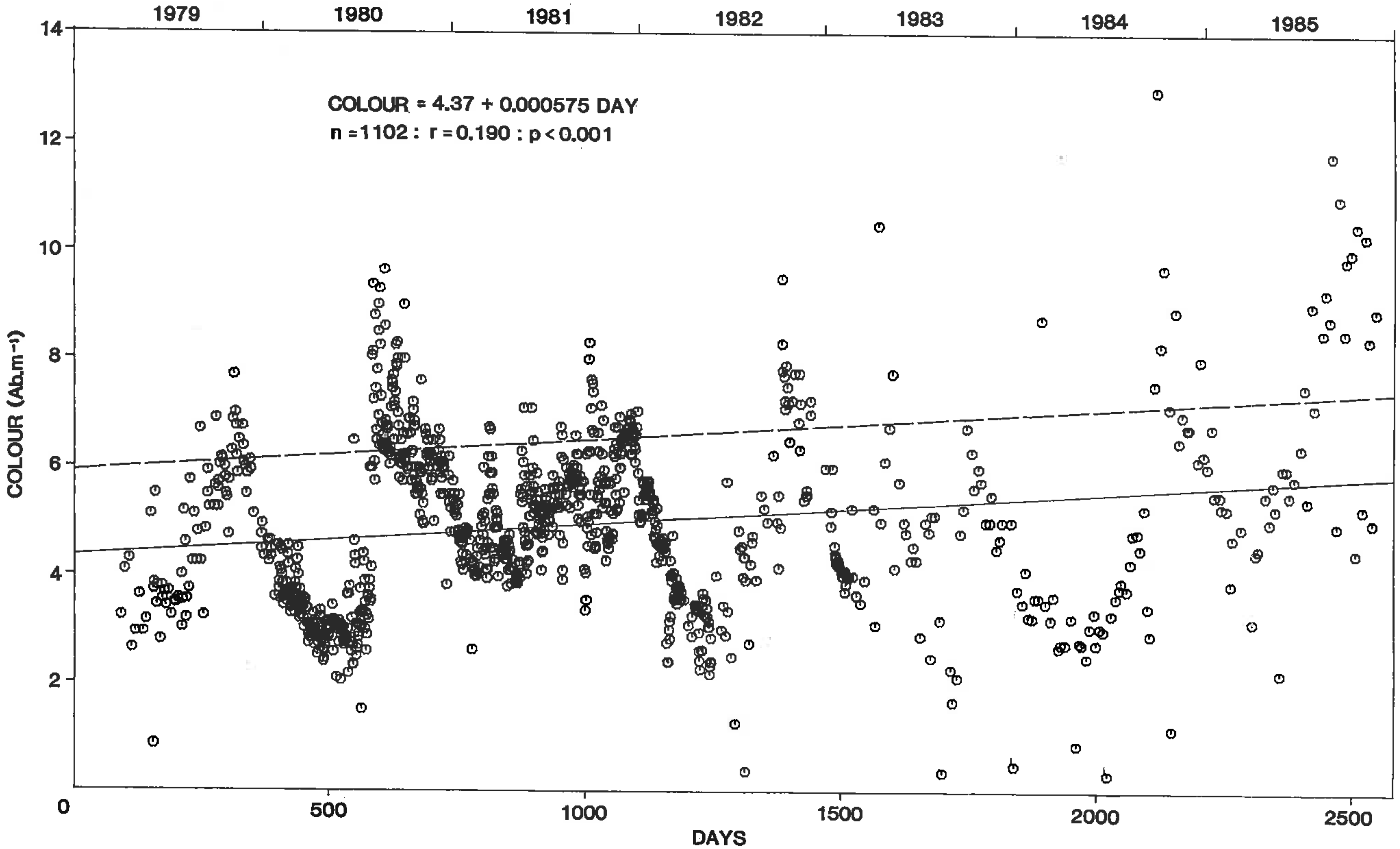


Figure 2 Colour in raw waters received at Chellow Heights treatment works April 1979 to December 1985 (Dashed line is one standard deviation above the regression line.)

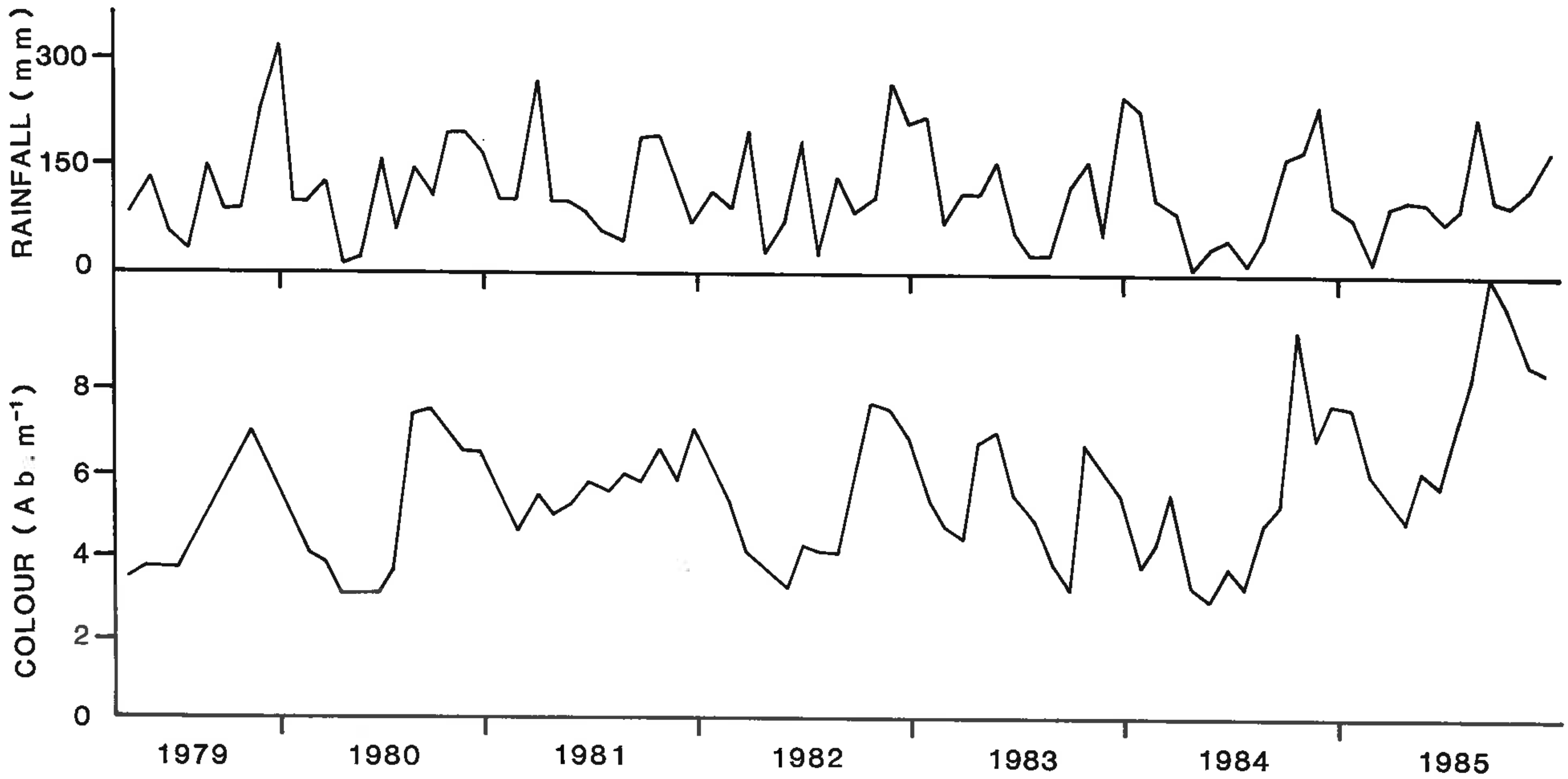


Figure 3   Pattern of total monthly rainfall and mean monthly colour levels from April 1979 to December 1985

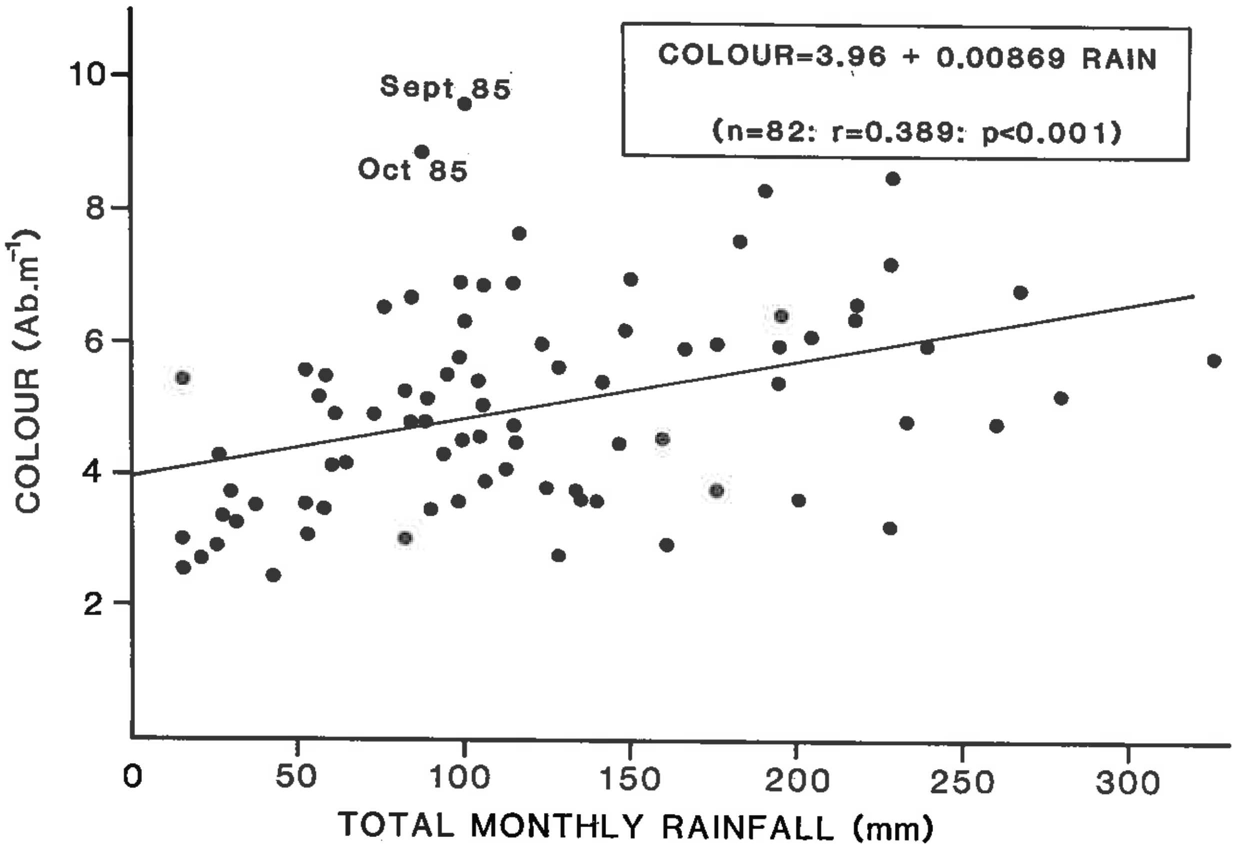


Figure 4 Mean monthly colour levels against total monthly rainfall

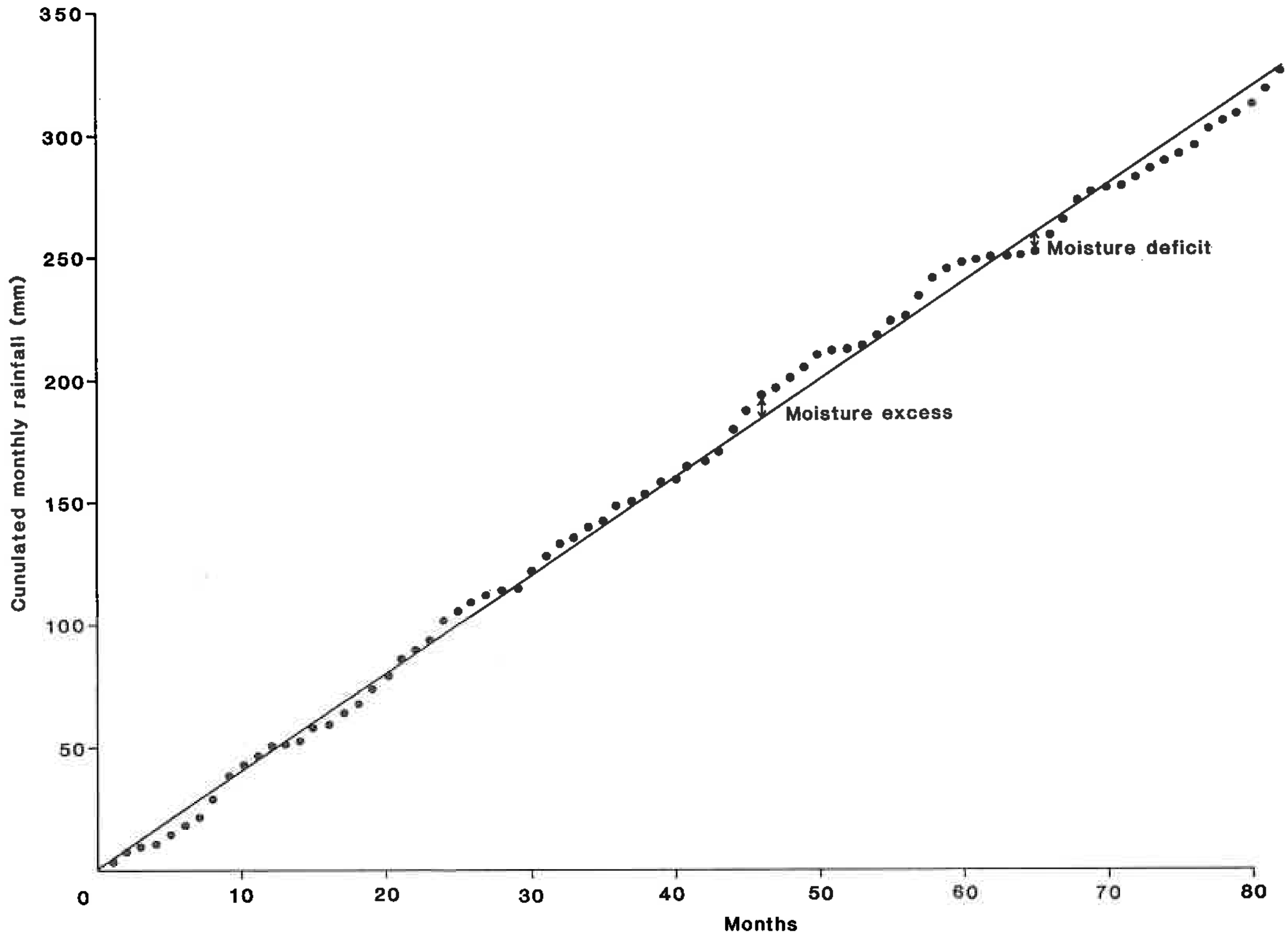


Figure 5  Graph illustrating derivation of moisture variations

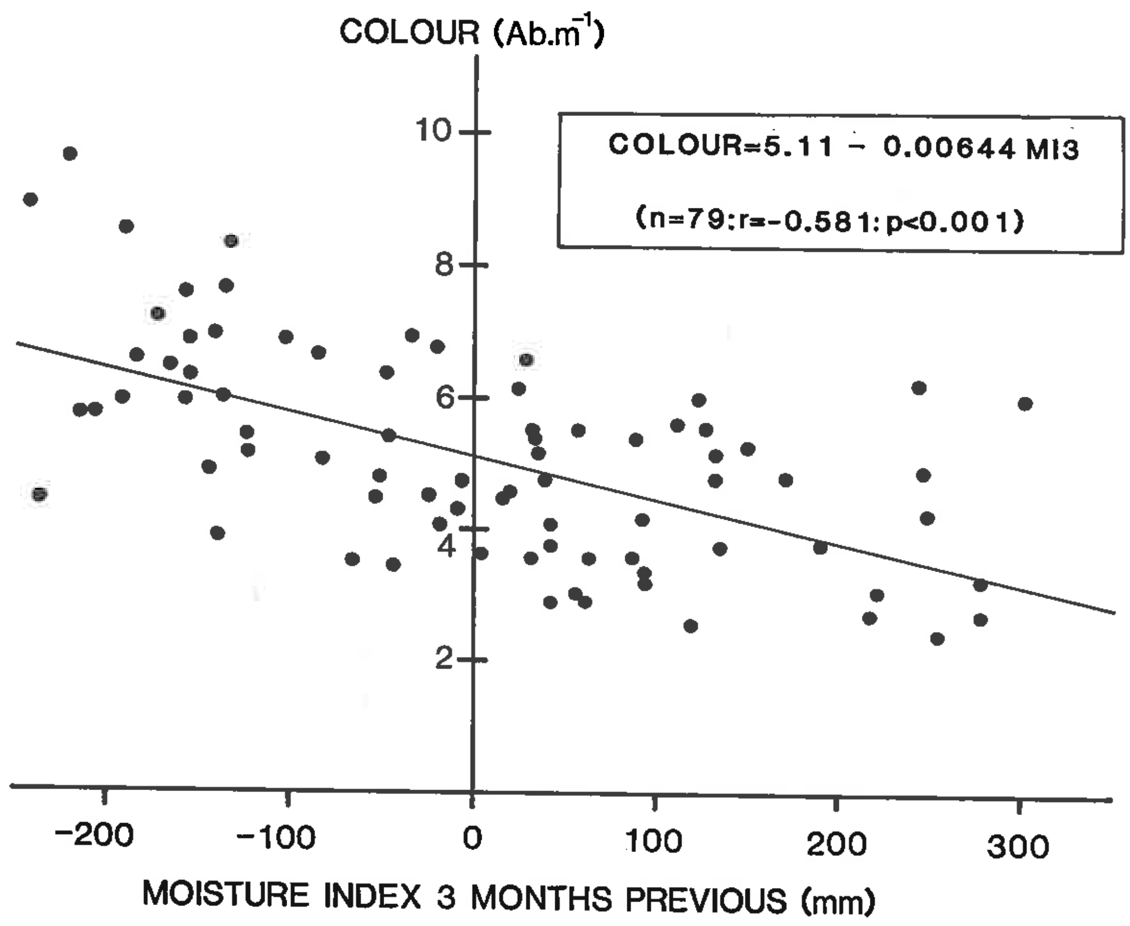


Figure 6 Mean monthly colour level against moisture index three months previous

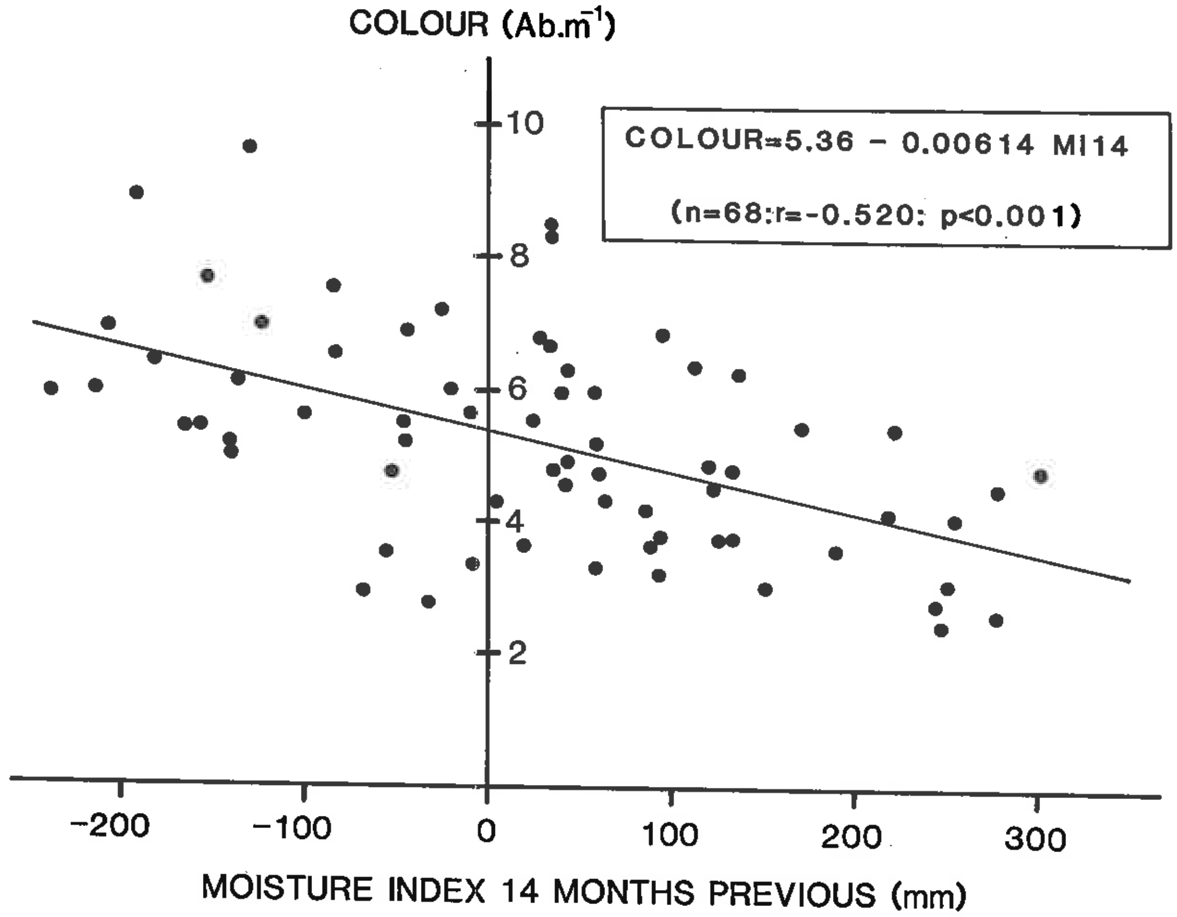


Figure 7 Mean monthly colour level against moisture index fourteen months previous

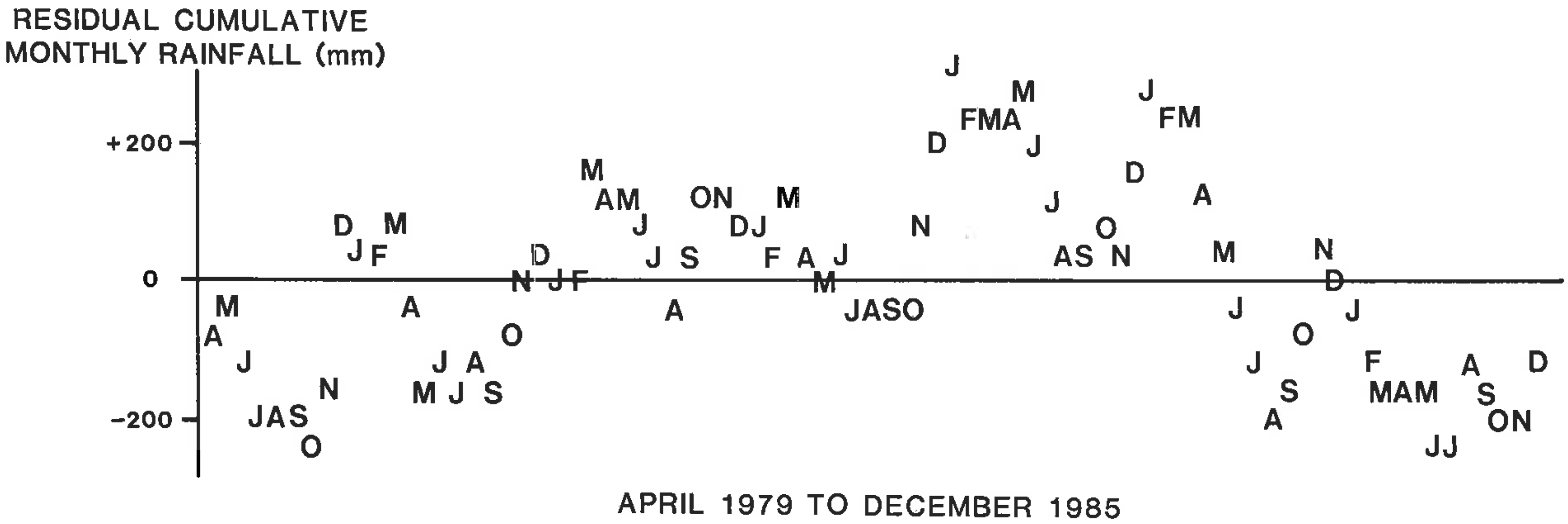


Figure 8 Pattern of moisture index from April 1979 to December 1985