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Changes in stream nitrate concentrations due to land management practices, ecological succession, and climate: Developing a systems approach to integrated catchment response

F. Worrall

Department of Geological Sciences, Science Laboratories, South Road, Durham, UK

W. T. Swank

Coweeta Hydrologic Laboratory, Southern Research Station, USDA Forest Service, Otto, North Carolina, USA

T. P. Burt

Department of Geography, Science Laboratories, South Road, Durham, UK

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[1] This study uses time series analysis to examine long-term stream water nitrate concentration records from a pair of forested catchments at the Coweeta Hydrologic Laboratory, North Carolina, USA. Monthly average concentrations were available from 1970 through 1997 for two forested catchments, one of which was clear-felled in 1977 and the other maintained as a control. The time series were decomposed into their trend and annual cycle before modeling as an autoregressive (AR) process. AR models were calculated for both an expanding and a shifting window so that prefelling could be directly compared with the effects of tree clearance. In comparison with flow records for both of the catchments, transfer function-noise models were calculated on a moving window basis, and the impulse functions were derived. Analysis shows that both catchments show an annual memory effect but that the clear-felled catchment shows, in addition, a 6-month memory effect. The annual effect in the control catchment responds to drought conditions while in the felled catchment, it reflects the change in vegetation. The 6-month effect in the felled catchment responds to drought conditions independent of both the annual effect and of logging operations. The control catchment shows no significant impulse function with respect to flow, while for the felled catchment a distinct impulsivity develops over time subsequent to logging and coincident with the onset of nitrogen saturation. By examining the nature of the nitrate export, rather than solely the levels of export, a systems approach can be taken to understanding catchment behavior. Such an approach shows that the catchment is in metastable equilibrium with respect to its hydrological pathways and nitrogen reserves but in dynamic equilibrium with respect to long-term temperature change. The onset of nitrogen saturation may represent irreversible changes in the catchment behavior, and impulsivity, with respect to streamflow, represents a new indicator of N-saturated conditions. *INDEX TERMS:* 1871 Hydrology: Surface water quality; 1803 Hydrology: Anthropogenic effects; *KEYWORDS:* nitrate, streamwater, forest hydrology, climate change, ecological change

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1. Introduction

[2] Nitrate concentrations in surface and groundwaters continue to be a matter of concern throughout the developed world [*Burt et al.*, 1993]. As a result of this concern, spatial and temporal variations of nitrate concentrations in catchments have been analyzed in order to help understand nitrate export from river basins. The export of nitrogen from forested catchments has been well studied with the identification of N saturation, where N availability exceeds in-situ, biological demands with consequent increases in N export and possible detrimental consequences on water quality and aquatic ecosystems [*Aber et al.*, 1989; *Stoddard*, 1994]. N saturated conditions could be a result of increased atmospheric deposition in Europe and the USA [*Aber et al.*, 1997; *Emmett et al.*, 1995]. The link between atmospheric deposition and N export has led to the extension of the critical loads concept [*Bull*, 1991] to nitrogen loads and its role in acidification [*Murdoch and Stoddard*, 1992; *Stoddard*, 1991] and eutrophication [*Emmett and Reynolds*, 1996]. Such saturation has been induced experimentally to

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understand response dynamics [*Adams et al.*, 1997; *Reynolds et al.*, 1998].

[3] Interest in forest nutrient dynamics has been used to evaluate the long-term role of management [*Knoepp and Swank*, 1997]. Particular attention has focused on the effects of tree harvesting [*Reynolds et al.*, 1995; *Romanowicz et al.*, 1996; *Neal et al.*, 1998a, 1998b; *Kamari et al.*, 1998], the comparison of harvesting techniques *Mann et al.*, 1988; *Lundborg*, 1997] and the management of riparian zones within forests [*Cirmo and McDonnell*, 1997]. Ecosystem changes have been considered, including: climate changes [*McNulty et al.*, 1997], forest fire [*Vose et al.*, 1999], and insect infestations [*Swank et al.*, 1981].

[4] The interest in nitrate cycling and nutrient response to external drivers means that many time series of data have been collected and examined. Several studies have examined the trend in records. *Arheimer et al.* [1996], examining forested catchments in Scandanavia, showed that although strong correlations with flow were recorded, the strongest effect on nitrate concentration was the relative length of the growing and dormant seasons. Also working in Scandinavian catchments, *Stålnacke et al.* [1999] showed that increases in the nitrate concentration trend were more closely related to reductions in phosphorus concentrations than nitrogen saturation. *Reynolds et al.* [1992] showed that although the trend in nitrate levels following a severe drought was unaffected, the amplitude of the annual cycle was increased and took several years to recover to pre-drought levels. *Creed et al.* [1996] explained the annual nitrate export from a forested catchment in terms of a flushing hypothesis [*Hornberger et al.*, 1994], and a similar explanation was used by *Edmonds and Blew* [1997]. *Swank and Vose* [1997] compared nitrate export trends and seasonal variations for a range of experimental catchments within a basin undergoing a range of management practices. They showed that saturation levels were related to intensity of management, with the highest saturation states correlating with the most disturbed watersheds. However, little work has been conducted on the nature of the export rather than the export itself. *Worrall and Burt* [1999], working in agricultural catchments, showed that the trend and the seasonal cycle were not the only components of a nitrate time series that could be analyzed. Detailed time series analysis can provide additional information on the nature of export and catchment response to external and internal drivers (e.g., climate change and land use management) that is not available by other approaches.

[5] Analysis of time series by autoregressive modeling [e.g., *Mann and Wald*, 1943] has revealed that the export of nitrate from a catchment shows a memory effect [*Naden and McDonald*, 1989]. This memory effect is a form of persistence, with the previous condition of nitrate export in the catchment influencing present nitrate export. Differing catchments show a range of memory effects, which for nitrate time series typically approximate to annual and diennial effects, with differing scales of significance. In catchments where multivariate records are kept, i.e., a range of chemical and physical parameters are recorded, then comparisons between these time series enables an understanding of not only how nitrate export responds to changes, both internal and external to the catchment, but also how the responsiveness of the nitrate export changes. Long nitrate records can be linked to long-term internal ecosystem controls on nitrate export and also can be used to track these changes over time to understand how they respond to external factors, e.g., climate change. Such detailed records are available from the catchments of the Coweeta Hydrologic Laboratory, North Carolina, USA. The number and diversity of long-term catchment experiments being conducted at Coweeta provide a foundation for comparing both managed and unmanaged catchments.

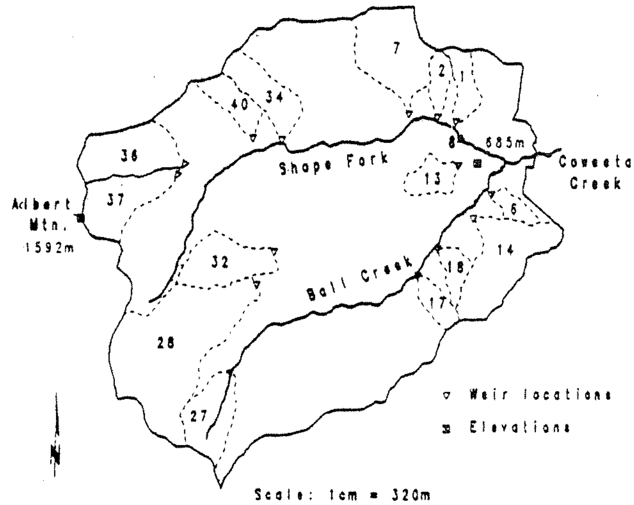

Figure 1. Location of the Coweeta laboratory with locations of experimental and reference catchment used in this study.

[6] The examination of long-term nitrate export records not only aids understanding nitrate behavior but also allows us to take a systems approach to catchment behavior. This approach is embodied in the raison d'etre of the Coweeta experiment: that the quantity, timing, and quality of streamflow provide an integrated measure of the success or failure of land management practices [*Swank and Crossley*, 1988]. This study takes such an integrated approach to understanding how catchments respond to external and internal drivers.

2. Methodology

2.1. Site Description

[7] The time series of nitrate concentrations analyzed here originate from the Coweeta Hydrologic Laboratory, North Carolina, USA. Established in 1934, the Coweeta watersheds represent one of the longest continuous environmental studies presently available. The 2185 ha watershed is divided into two adjacent basins (Figure 1). The climate of the region is classified as marine, humid temperate [*Swift et al.*, 1988]. Mean annual precipitation varies from 1800 mm at low altitudes in the basin to 2500 mm at the highest altitudes, with March typically being the wettest month and snowfall making up less than 5% of the precipitation. Mean annual temperature is 12.6°C at the base station, with an average monthly low of 3.3°C in January and a high of 21.6°C in July. The geology of the basin is dominated by metamorphic formations including schists, gneisses and metasandstones [*Hatcher*, 1988]. Soils fall into two orders: immature Inceptisols and older, mature

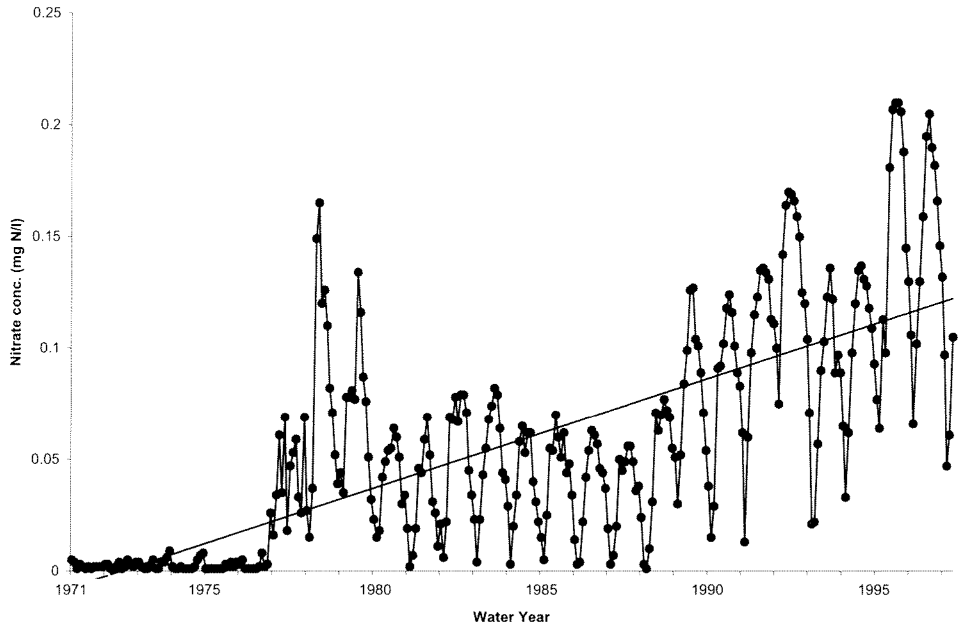

Figure 2. Nitrate concentrations in the Big Hurricane stream (the felled catchment) in comparison to the best fit linear trend.

Ultisols. Steep faces at high elevations are covered by the umbric dystrochrepts of the Porter series, the remaining Inceptisols are of the Chandler gravelly loam series. The Ultisols comprise typic hapludults and humic hapludults. Typic hapludults cover the largest area of the basin and consist of the Coweeta-Evard gravelly loam and Fanin sandy loam series. Mixed mesophytic forests characterize the region and the four major forest types of the basin have been described by *Day et al.* [1988].

[8] This study focuses on the nitrate concentrations observed in a pair of catchments, 2 and 7; the nitrate time series are shown in Figures 2 and 3, respectively. Catchment 2 (Shope branch) is 12 ha in area with a maximum elevation of 1004 m. Catchment 7 (Big Hurricane) is 59 ha in size and reaches a maximum elevation of 1077 m. The two catchments are adjacent and have similar southerly aspects (Figure 1). Catchment 7 was commercially clear-felled, cable logged and allowed to regenerate in 1977 and is hence forward referred to as the felled catchment [*Swank et al.*, 2001]. As part of logging operations, 3 contour roadways were constructed traversing the catchment at 300m intervals. Catchment 2 is one of the control catchments

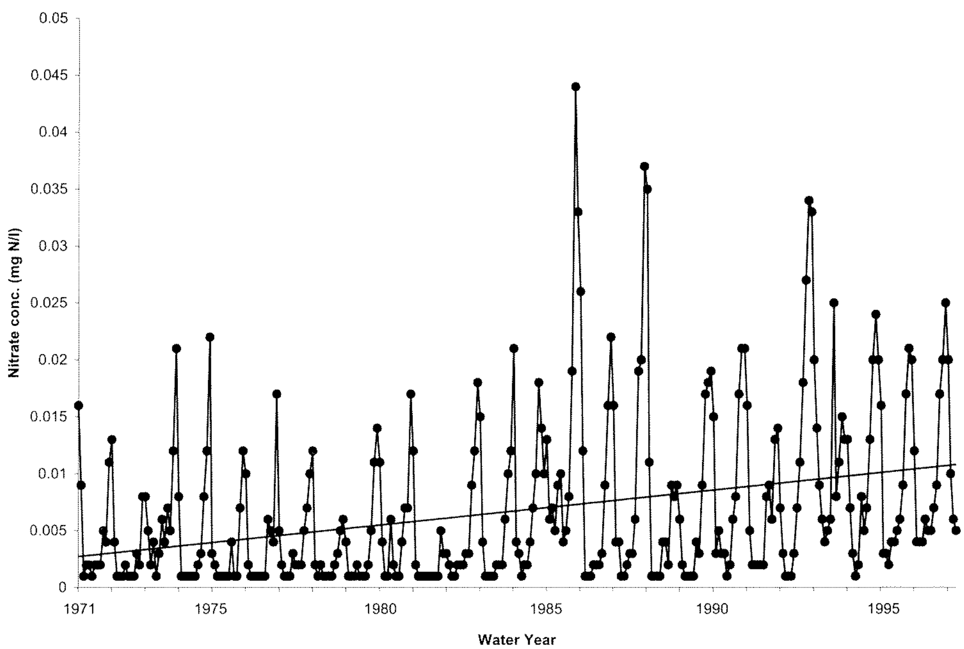

Figure 3. Nitrate concentrations in the Shope branch (control catchment) in comparison to the best fit linear trend.

within the basin and has remained undisturbed since 1927, it is henceforward referred to as the control catchment. Stream gauging on both these catchments commenced in 1934 and nitrate monitoring in 1972. Stream water is sampled weekly. Samples are immediately refrigerated and analyzed within 7 days. Before July 1990 nitrate was analyzed by automated cadmium reduction method and thereafter by ion chromatography. Quality control is maintained by analysis of standards from an independent laboratory. Weekly values are flow weighted to provide the monthly time series analyzed here.

[9] Stream discharge is measured continuously on each watershed using 90° V notch weirs. Equally, a range of meteorological conditions are monitored in the catchment that mean that results of time series analysis can be compared to detailed rainfall and temperature records.

2.2. Decomposition of Time Series

[10] There are a number of possible approaches to the analysis of nitrate time series [*Esterby*, 1997]. It is assumed in this paper that the monthly nitrate time series can be treated as a series of separable elements: the trend, the seasonal variation, and the residual [*Worrall and Burt*, 1998, equation 1]. This is a common approach to analyzing time series that views the time series as a deterministic (trend and seasonal components) and a stochastic component (the residual or error term) [*Gottmann*, 1981; *Harvey*, 1981]. This study focuses on the analysis of the residual, a component previously ignored in studies of nitrate export. The time series is decomposed into its trend and seasonal variation using a multiplicative model. A multiplicative model is preferred over an additive model because of the obvious nonstationarity in the time series from the felled catchment, i.e., the amplitude of the annual cycle appears to increase with the increasing trend in nitrate time series (Figure 2). The multiplicative model allows the seasonal indices to increase in line with the trend in the data.

$$Y(t) = a \times \text{trend} \times \text{seasonal variation} + \text{residual}, \qquad (1)$$

where Y(t) is the nitrate concentration over time and a is a model coefficient.

[11] Four alternative strategies were used for analyzing the trend in the data: linear trend, quadratic trend, exponential curve and S curve. The trend in the data is fitted using least squares regression and the series is detrended by dividing the data by the trend component as suggested by the multiplicative model given in equation 1. The seasonal variation is removed by use of seasonal indices. A centered moving average of length equal to that of the annual cycle is calculated. Indeed, in this particular case, because the annual cycle length is an even number (i.e., 12 months), the moving average is a two-step process in order to synchronize the moving average correctly. Once the moving average is obtained, it is divided into the detrended data to obtain what can be referred to as raw seasonals. Within each seasonal period, the median value of the raw seasonals is calculated. It is these medians that make up the seasonal indices. The mean of the medians is adjusted so that their mean is one; these seasonal indices are in turn used to seasonally adjust the data by dividing the detrended data by them. The seasonal indices approach is: more responsive to the actual data; brings fewer assumptions to the data than fitting simple harmonic functions derived from Fourier analysis; and is readily available in standard statistical analysis packages, e.g., Minitab (Minitab version 13.20).

2.3. Derivation of AR Models

[12] The first approach taken to the analysis of the residual was the Mann-Wald process [*Mann and Wald*, 1943; *Gottmann*, 1981]: this method calculates the best fit autoregressive (AR) model of the residuals. The Mann-Wald process is used because the identification of significant AR models is physically interpretable in terms of the processes of nitrate hydrology. The order of the AR model was systematically varied using both a step-up and a step-down procedure so as to avoid local minima in the model fit. The fit of the model was checked using the Quenouille method [*Quenouille*, 1947]. AR(p) (where p is the order of the model) was initially calculated for both series in their entirety for $p \leq 18$ in order to identify significant AR models that could be tracked to understand their variation over the period of sampling. Six month and annual memory effects have been previously identified in water quality time series from a range of settings including nitrate time series [*Worrall and Burt*, 1999] and dissolved organic carbon time series [*Naden and McDonald*, 1989], and so these effects were particularly focused on.

[13] After identifying significant memory effects for the whole sequence, the variation in these effects are tracked in two ways. The first is to calculate the AR(p) (where p is the order of the model found to be significant for the entire series) for a subset of the concentration record. The subset starts at the beginning of the record and the model is then recalculated, but the subset is allowed to expand by a number of months equal to the annual cycle, i.e., expansion in 12 month steps: this process is iterated until the whole record is covered. Thus this method represents the calculation of the time series model for an expanding window across the record. The initial length of the subset used in this study was set at 72 months. The longer this subset, the greater the opportunity for discerning significant effects. However, it was felt important to study the prefelling period, and thus the length of the subset was constrained by the length of record prior to the clear felling in 1977.

[14] The second method is to use a shifting window. In this case the subset of the record for which the AR(p) model is to be calculated is set at a fixed length. The model, at the chosen value of p, is calculated for this length of subset starting at the beginning of the record. The model is recalculated for the same length of subset, but the subset is shifted by the length of the annual cycle and this process is iterated until the end of the record is reached. In this way the time series is being calculated for a shifting, as contrasted to an expanding, window. The length of the shifting window is again set to 72 months so as to encompass the whole period prior to clear-felling of the felled catchment. In both the shifting and expanding window methods the year referred to is the year at the end of the period being examined, e.g., in the subsequent discussion 1977 refers to the result for the previous six years, the period 1971–1977.

[15] By calculating the AR models for expanding and shifting windows multiple comparisons are being made and significance tested. Making such comparisons increases the possibility of familywise error rate and it would certainly be

larger than the nominal 5% probability value if the 95% significance level is chosen. To minimize the familywise error rate comparison is also made with the 99% significance level in the Quenouille test.

[16] Results from both shifting and expanding windows can be compared to meteorological conditions prevailing in the catchment. A range of measures of the rainfall and temperature can be used to examine the effect of external climatic drivers on the catchment nitrate response in comparison to clear-felling and the vegetational succession resulting from the forest regrowth.

[17] There is an assumption of homoscedasticity made in this approach to AR modeling. This assumption is particularly important if the goal is to provide a predictive model of nitrate export, where an allowance for conditional heteroscedasticity (ARCH [*Bollersley*, 1986]) would probably give better predicitve power. However, the goal of this research is to use AR modeling to examine long-term catchment memory effects in the context of internal and external driving variables: Thus an allowance for conditional heteroscedasticity would obscure the results while conclusions from our analyses are valid. Similarly, a nonlinear filter (e.g., Kalman filter) may well provide further information in understanding nitrate concentrations; however, the calculation of the AR model by using a shifting window means that changes during the course of the period of observation can be tracked. The use of both shifting and expanding windows of time enables an estimate of the scale and time constants of effects to be made.

2.4. Derivation of the Impulse Function

[18] Transfer-function noise models (TFN) were calculated for both catchments against the streamflow record. The first stage of calculating the TFN model is to derive an autoregressive integrated moving average (ARIMA [*Box and Jenkins*, 1970]) model of the input series, in this case the flow record. The model is derived using the method of *Shumway* [1988]. Because the nitrate time series (the output series) has been decomposed rather than differenced, the input series was treated similarly and so the model derived was in fact an ARMA model. To identify the order of the ARMA model the autocorrelation function (ACF) and the partial autocorrelation function (PACF) of the residuals from the decomposition of the input series were examined. In a series already made stationary, the number of significant lags in the PACF is taken as an estimate of the order of the autoregressive component of the ARMA model. The order of the moving average component was estimated in a similar fashion from the ACF. The necessity of allowing for seasonal autoregressive or seasonal moving average behavior can also be identified from the PACF and ACF respectively. The fit of the estimated ARMA model for the input series was tested by systematically varying the order of the AR and MA components to test the sufficiency of the fit. In this case, calculating the variance of the residuals after fitting the particular ARMA model was used as a measure of the model fit. Once the ARMA of the input series has been calculated satisfactorily, this ARMA is used to filter the output series (the nitrate record). The cross-correlation function can then be calculated between the residuals of the input and output series; the result is the impulse function. The impulse function represents a measure of how responsive the output is to the input above and beyond that which can be explained by the other components of the time series, i.e., the trend, seasonal cycle and the ARMA component. In the case being studied here it represents how an unpredicted flow, i.e., that not predicted by the other components in the time series analysis, influences the nitrate concentration? If concentration/discharge relationships were calculated these would reflect seasonal differences and the memory effects highlighted by AR modeling. It is once a range of other components have been removed that the link between discharge and concentration can be properly explored in terms of how an impulse in one reflects changes in the other time series.

Table 1. Residual Variance of the Time Series After Removal of the Components of the Time Series Model[a]

Component	Control Catchment	Felled Catchment
Trend		
Linear	90	47
Quadratic	90	45
Exponential curve	91	60
S curve	99	47
Seasonal		
Additive	41	33
Multiplicative	39	28
Autoregressive		
Diennial	15	21
Annual	15	21

[a]For the control catchment the diennial autoregressive component is a AR(6) and the annual effect is AR(12). For the felled catchment the diennial autoregressive component is AR(7) and the annual effect is AR(13).

[19] This approach to the derivation of an impulse function is valid when the input and output series are independent of each other and when causal feedback can be discounted. The significance of the cross-correlations was tested using a t-test. Because of the problem of multiple comparisons increasing the familywise error rate the results are also tested against the 99% significance level. As with the AR modeling, the impulse function was calculated for both expanding and shifting windows across the record as a means of tracking the change in impulsivity of the catchments in response to natural and external drivers. This approach to understanding relation between variables creates a reliable and unbiased measure of the relation and reduces problems of autocorrelation between the series [*Gurnell et al.*, 1992].

3. Results

3.1. Time Series Decomposition

[20] Fits of the alternative approaches to the fitting of the trend, as assessed by the percentage of the original variance explained, showed that the fit of both the linear and the quadratic trend performed better than either the exponential curve or an S curve for both the felled catchment and the control catchments (Table 1). The fitting of the quadratic trend gave a 2% improvement in fit for the felled catchment in comparison to the fit of the linear trend and less than 0.5% improvement in fit for the control catchment, as a result the simpler linear trend was retained (Table 1 and Figures 2 and 3). Long term trends in the data have been discussed by *Swank and Vose* [1997] and the correlation between nitrogen export from the catchment and the nitro-

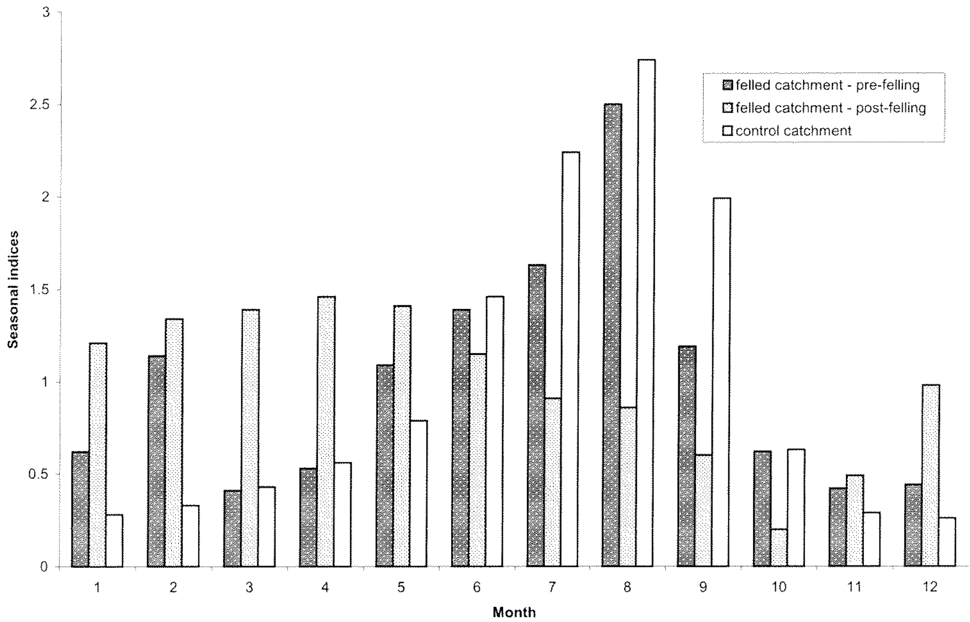

Figure 4. Seasonal indices for the control catchment and the felled catchment prior to and after felling.

gen content of the soils and biomass have been discussed by *Knoepp and Swank* [1997] and *Elliot et al.* [2002], and these will not be discussed further here.

[21] Seasonal decomposition by an additive model improves the fit of model by 49 and 14% for the control and felled catchments, respectively (Table 1). The use of a multiplicative model improves the fit of the model by 51 and 19% over the fit of the linear model for the control and felled catchments, respectively (Table 1). The seasonal indices from control catchment show a marked asymmetry in the annual response (Figure 4). The peak nitrate concentration occurs in August with a minimum in the winter months. The cycle shows a sharp peak and a broad, flat trough. This pattern is very similar to that for that prefelling in the felled catchment (Figure 4). This contrasts with the pattern from the felled catchment postfelling where the peak of nitrate concentration has shifted to April and the minimum to October (Figure 4). Moreover, the shape of the response has shifted, with a broad, flat, symmetric peak during the periods of winter and spring and a sharp, symmetric trough during the autumn months. The decomposition was performed for the whole series including both precutting and postcutting, though the result will be dominated by the postcutting period.

3.2. AR Modeling

[22] For the control catchment, analysis of the whole series showed that a significant annual effect exists, but no 6-month effect could be discerned (data not shown). The 12-month effect was positive, i.e., it acts to increase nitrate concentrations in the present month. The 12-month effect was shown by both expanding and shifting window analyses. The magnitude of the memory effect is taken as the magnitude of the pth coefficient in the AR(p) model (a_p), the significance of the effect is then judged relative to the magnitude of the pth coefficient that shows a 95% probability of being significantly different from zero as calculated by the Quenouille method ($a_{p'}$). Therefore values are quoted as the ratio $a_p/a_{p'}$ where a_p is the pth coefficient of the AR(p) model and $a_{p'}$ the coefficient that has a 95% probability of not being zero for that model: a value of $a_p/a_{p'} > 1$ indicates a significant result at the 95% level. In the case of the control catchment the magnitude of the twelfth coefficient of the best fit model is compared to the magnitude of the twelfth coefficient that would be significantly different from zero (at the 95% level) for that length of series. The fit of an autoregressive model improves the fit of the time series model by 24% over the fit of the multiplicative model for the control catchment (Table 1). The residual after removal of the annual effect illustrates that after model development only 15% of the original variance remains unexplained (Figure 5) and residuals are normally distributed (Figure 6).

[23] Assessing the time series for the control catchment using an expanding window (Figure 7) shows two peaks in the memory separated by a significant disappearance of the memory with a decline in the memory toward the end of the record. The transition back to a significant memory corresponds to the onset of the severest drought in the catchment during the period of the record. However, the lowest point of the drought corresponds to the peak in the memory in 1987. As this is an expanding window perspective, an effect must be large, short-lived and dominate the calculated memory in the following years. This suggests that the drought is marked by an initial decrease in memory and then a rapid return. This might well be expected if the possible response to a change in state is considered. If the change is sufficiently large, then that year will have no relation to the previous and hence memory effects decline rapidly. *Burt et al.* [1988] and *Reynolds et al.* [1992] show that the effect of drought in different environments (agricultural and moorland) is to cause increased nitrate runoff in the year after a severe drought. This effect could not be accounted for in the trend or seasonal variation of the series so will remain into the residual and be part of the AR analysis. Hence a large positive response recurs in years

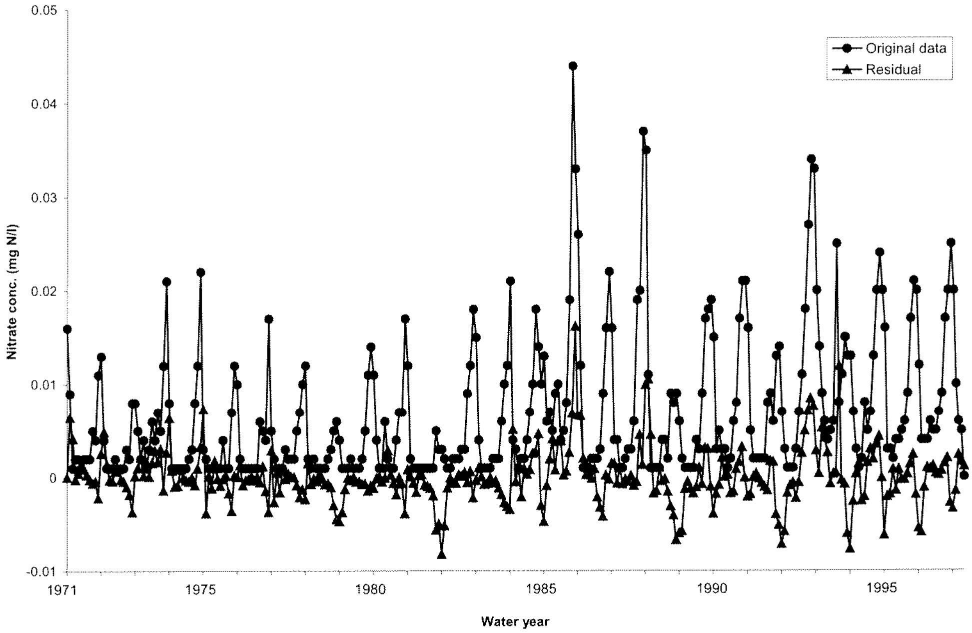

Figure 5. The original data for the control catchment in comparison to the residual time series after removal of the linear trend, seasonal indices, and AR(12).

subsequent to the onset of drought. This mechanism implies that response to drought may-be nonlinear. There are dry and wet years throughout the period of the record, but only the driest years cause a distinct response. The decrease in memory in 1994 (month 276) must also be a large single year effect.

[24] The shifting window analysis for the control catchment (Figure 8) shows more detail of the response to the drought with the peak in memory occurring near the start of the drought with a decreasing memory effect in the years preceding the drought when annual rainfall is increasing.

[25] For the felled catchment, analysis of the whole series shows both a significant diennial and annual effect. However, these effects manifest themselves as a 7-month effect and a 13-month effect. Also, in this catchment the annual (13-month effect) has a significant negative effect, and conversely the diennial effect is positive. This is the reverse of that observed in the control catchment. The fit of an autoregressive model improves the fit of the time series model by 7% over the fit of the multiplicative model for the felled catchment (Table 1). The residual after removal of the annual effect illustrates that after model development only 21% of the original variance remains unexplained (Figure 9).

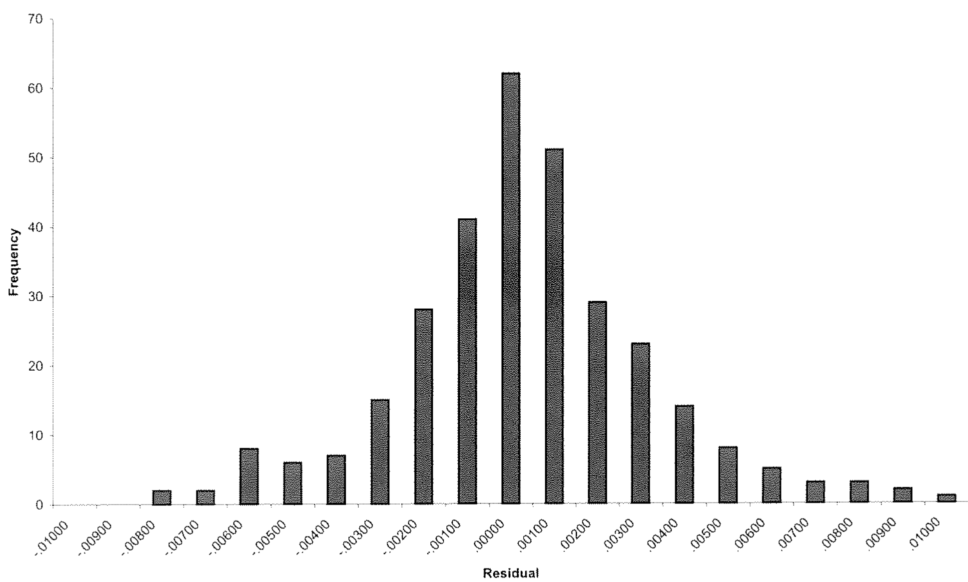

Figure 6. The distribution of residuals from the control catchment after the removal of the linear trend, seasonal indices, and AR(12).

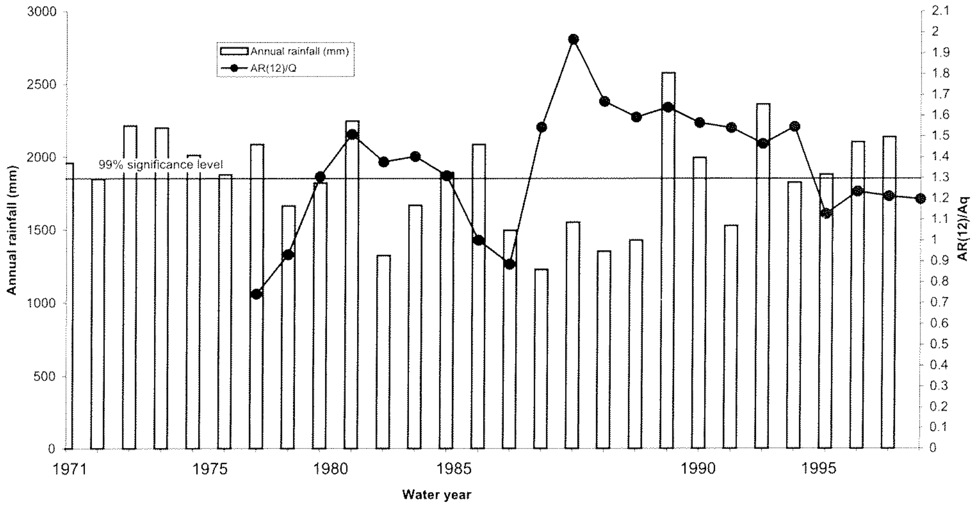

Figure 7. The scale and significance of the annual memory effect for the control catchment, calculated for increasing time periods (expanding window) as $a_p/a_{p'}$ over the period of observation for the control catchment, where p = 12, and $a_{p'}$ is Quenouille test statistic at the 95% level, with the 99% level illustrated. The year refers to the year at the end of the calculation period.

Both the annual and diennial effects were investigated as expanding and shifting windows.

[26] The diennial month effect, followed with an expanding window (Figure 10) shows that the memory is significant throughout the period of the record. Following clear-felling in the 72nd month of the record, a sustained rise in the magnitude of the diennial memory effect is observed until 1992 after which a decline is observed at the end of the record. In comparison to the prevailing climatic conditions, this trend shows no relation with the annual precipitation, but rather a good visual correlation with the annual average temperature. Analyses using average temperature for either the growing or the dormant season do not improve this comparison. The clear-felling of the felled catchment coincides with lowest average temperature over the period of the study and precedes a 15 year rising trend in temperature. The expanding window technique is relatively conservative and events that affect only one year of the record will be severely damped out by the other years being considered. This means that only long-term effects will have a significant and lasting affect on the catchment memory as viewed in an expanding window. Since the window expands, the effect on the memory would diminish if the year-on-year effect were constant. The magnitude of the memory in this case diminishes, and the peak of the effect (1992) lags behind the maximum in the annual average temperature (1991). This implies a linear affect of average temperature on catchment nitrate memory.

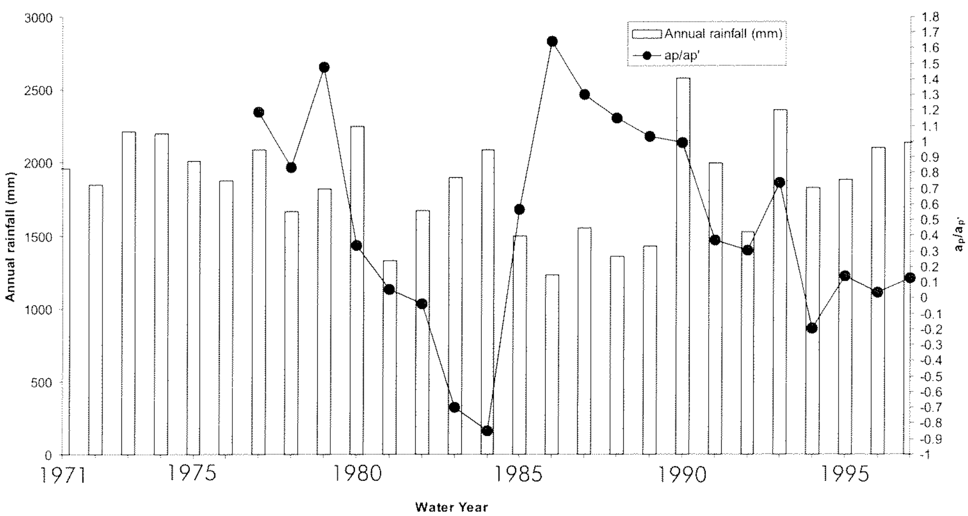

Figure 8. The scale and significance of the annual memory effect for the control catchment, calculated for overlapping time periods (shifting window) as $a_p/a_{p'}$ over the period of observation for the control catchment, where p = 12, and $a_{p'}$ is Quenouille test statistic at the 95% level, with the 99% level illustrated. The year refers to the year at the end of the calculation period.

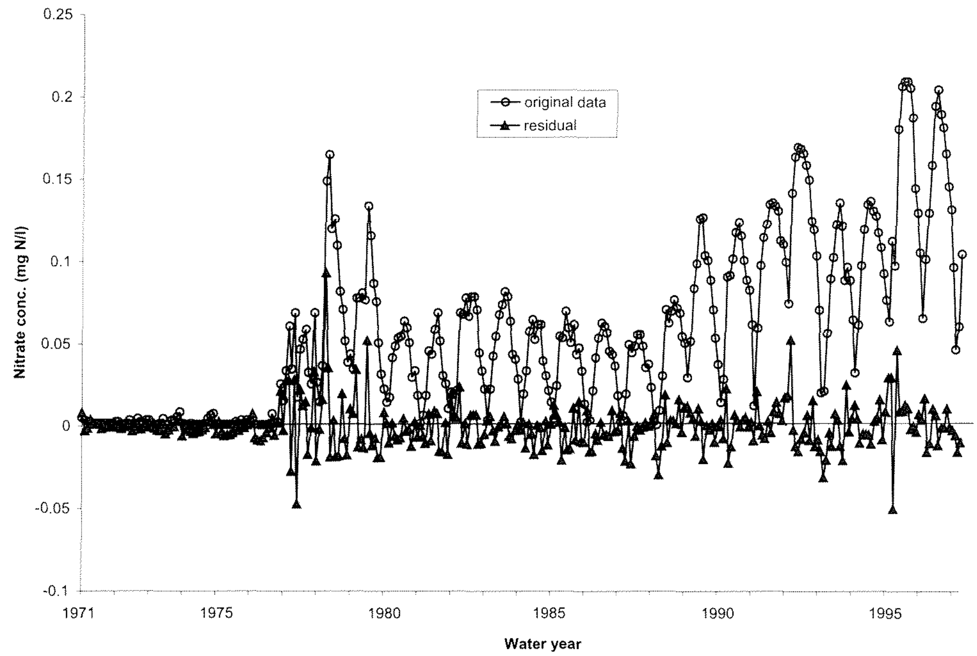

Figure 9. The original data for the felled catchment in comparison to the residual time series after removal of the linear trend, seasonal indices, and AR(13).

[27] For the shifting window analysis, a clear differentiation between the memory effects can be observed (Figure 11). The annual memory (13 month) is significant before the clear-cutting and returns 10 years later. The annual memory when significant (significance is still judged against the 95% level) is negative: this means that the nitrate concentration in the present month experiences a dampening effect due to the nitrate concentrations a year previous. The effect not only decreases it also switches its sign, although care must be taken in interpreting effects that cannot be shown to be significant at the 99% level. The switch in the annual memory between 1976 and 1977 can be associated with the effect of clear-cutting a change that cannot be associated with either precipitation or temperature. However, there is an equally sharp switch after 1987, but again this change cannot be associated with climatic drivers and so this switch must be associated with ecological changes in the nitrogen pool. Approximately ten years into forest succession the black locust (*Robinia pseudo-acacia*) dies back due to insect infestation [*Swank et al.*, 2001]. Black locust is an abundant nitrogen fixing legume in regenerated southern Appalachian forests, with fixation rates estimated to average 10 kg N $ha^{-1}a^{-1}$ on the felled catchment early in the regrowth [*Boring and Swank*, 1984]. Thus the die-back of black locust changes the nature of the nitrogen reserves and creates an additional source of nitrogen in the soil and from

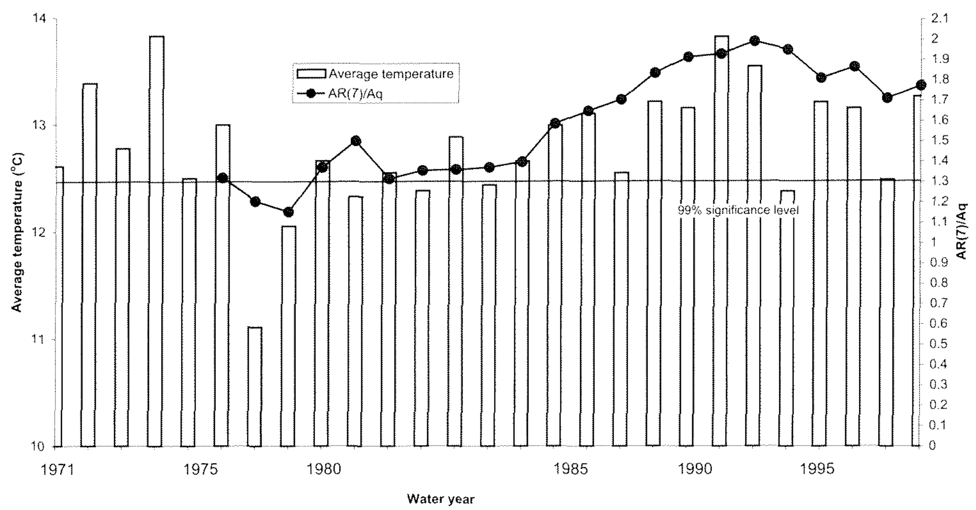

Figure 10. The scale and significance of the dienniel memory effect for the felled catchment, calculated for increasing time periods (expanding window) as $a_p/a_{p'}$ over the period of observation for the control catchment, where p = 7, and $a_{p'}$ is Quenouille test statistic at the 95% level, with the 99% level illustrated. The year refers to the year at the end of the calculation period.

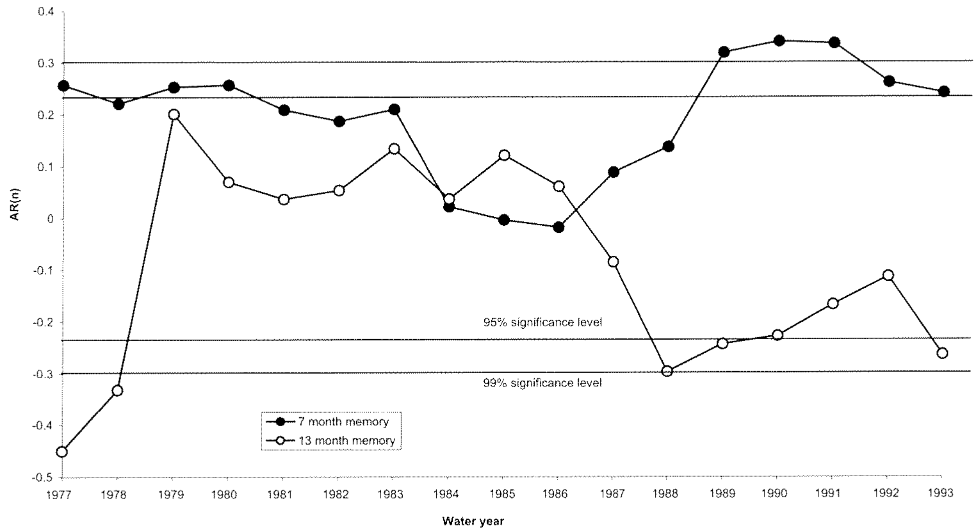

Figure 11. The scale and significance of the dienniel and annual memory effects for the felled catchment, calculated for overlapping time periods (shifting window). The pth coefficient, a_p over the period of observation for the felled catchment, where p = 7 and 13, in comparison to the 95% and 99% significance levels, the length of overlapping time period of 72 months. The year refers to the year at the end of the calculation period.

the decomposition of woody material. The contrast with clear-felling is that whereas clear-felling causes the memory effect to disappear, the die-back of black locust causes the memory effect to return.

[28] If it is assumed that a certain amount of memory can be ascribed to any given annual cycle, i.e., that one year shows a more significant memory for previous concentration than does another, it is possible in a qualitative sense to invert these patterns to understand the nature of the signal that caused them. Because this was calculated on a 6-year moving window basis, an effect in a single year would have an apparent effect over a 6 year period. If the response to clear-felling was limited to a single year then a step change in the moving window response would be observed and would last for approximately six years. The effect observed here lasts for at least ten years implying a response of at least five years duration. If the response lasted for more than one year but had a diminishing effect then this would also have a diminishing effect on the shifting window response, but any diminishing response would have a minimum time constant of six years. In this case, the reversion of the annual memory takes at most 3 years (1984–1987). This implies that there is a distinct reverse effect to that of the clear-felling that can be ascribed to successional changes.

[29] The diennial memory follows a quite distinct pattern (Figure 11). There is no switching off of the memory effect upon the clear-felling of the catchment. The magnitude does decline gently, but changes dramatically after 1982. Comparison with the annual precipitation shows that the minimum memory response corresponds with the driest year during the study. Both catchments show a response to drought, but the response manifests itself differently between the two catchments.

3.3. Impulse Function

[30] The order of the ARMA models for the flow in the control catchment were ARMA (102), for the felled catchment they are ARMA (504). The PACF and ACF for the residuals of fitting ARMA (504) to the detrended and deseasoned series for the felled catchment show that the series show no significant lags at the 95% level and so the ARMA models can be viewed as a good fit leaving only white noise as a residual (Figure 12). The impulse function is plotted as the ratio of the cross-correlation coefficient calculated against the correlation coefficient that would be significantly different from zero at the 95% level for series of that length, e.g., a value ≥ 1 represents a significant result (the 99% significance level is also illustrated; Figure 13). No significant cross-correlations could be found in the impulse functions derived for the control catchment. Considering the entire record for the felled catchment, significant cross-correlations are observed at zero lag, i.e., the catchment responds impulsively to changes in stream discharge. Following the impulse function as a shifting window shows there is no significant impulse function prior to clear-felling (Figure 13). There is no significant effect until 1980, a lag of 3 years behind the clear-felling when the cross-correlation at zero lag becomes significant, i.e., the catchment develops impulsivity. This impulsivity, i.e., significant cross-correlation at zero lag, is the dominant feature of the impulse function across the record. The overall pattern is one of increasing impulsivity over the period of the record. Considering that a shifting window perspective tends to average out changes in the catchment, it is easy to see large changes in the impulsivity of the catchment. However, the impulsiveness of the catchment becomes stable toward the end of the study period.

4. Discussion

[31] The differences between the catchments are marked. The existence of an annual positive memory effect, as observed for the control catchment, has previously been ascribed to an increase in winter-summer rainfalls [*Worrall*

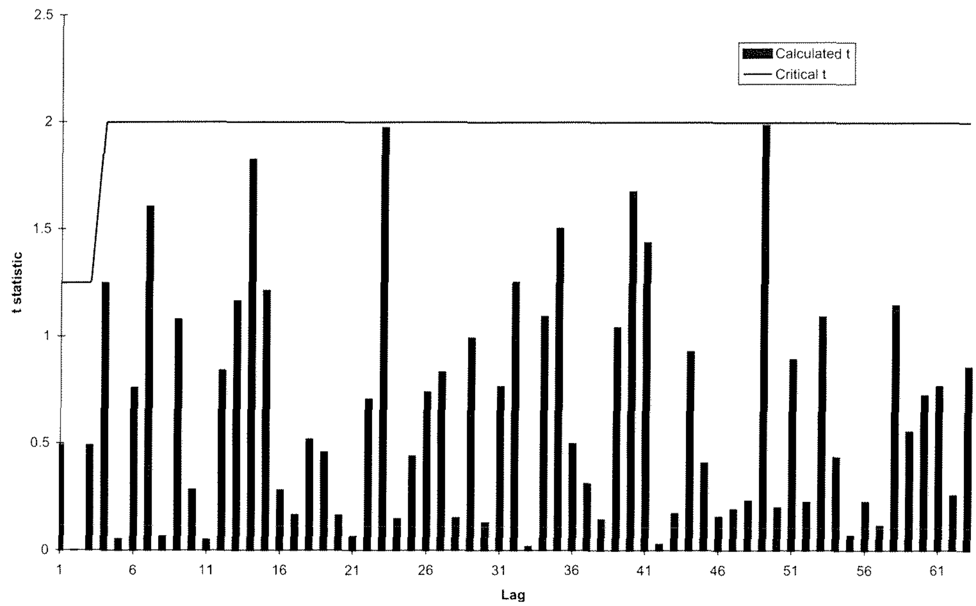

Figure 12. The calculated t statistic of the ACF and PACF in comparison to the critical value of the t statistic at the 95% level.

and Burt, 1999]. This cannot be the case here over a such a long period of time, but the scale of the effect is dependent on rainfall and especially the onset of drought conditions. An especially warm summer may stimulate nitrification and this would have the twin effects of increasing nitrate export above that expected as part of the overall or seasonal trends within the catchment, and perhaps stimulate primary production within that watershed. The increased primary production could carry over to the next summer as an increased pool of mineralizable organic matter if primary production were in the from of leaf, rather than wood production. The balance between export and utilization of available nitrogen would be critically dependent upon the balance of the hydrology and the nitrifiers. In a wet summer the balance would favor export of nitrate, but in a dry summer it would favor utilization and storage. The scale of any memory effect observed over the period of observation would then represent the nature of the juxtaposition and transition between wet and dry years.

[32] A similar approach can be used to explain the negative annual memory effect observed for the felled catchment. If relative increases in nitrification activity were exported from the catchment, rather than utilized within the ecosystem, then that increase in mineralization would have

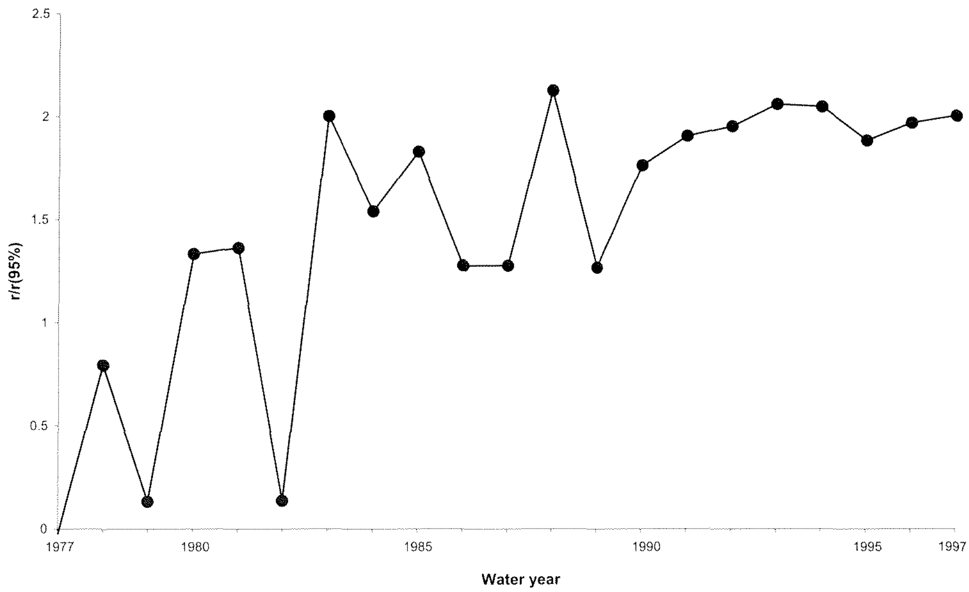

Figure 13. The zero-lag cross-correlation coefficient of the impulse function derived from the felled catchment, calculated for overlapping time periods (shifting windows), in comparison to the 95% and 99% significance levels with the length of the overlapping time period of 72 months. The year refers to the year at the end of the calculation period.

the effect of diminishing the pool of available nitrogen. A relative decrease in the pool of available nitrogen would then restrict productivity with the consequent effect for the size of available nitrogen for subsequent years. This shift in the balance of controls could result from either a different set of hydrological pathways operating in the felled catchment as opposed to the control catchment or a difference in composition of the soil microbial population - the former is more likely. It is important to note that the negative annual effect occurred prior to the clear-felling and returned later in the sequence; then the difference in balance between factors controlling nitrate between the catchment must be due, in this case, to innate differences between the catchments. A positive annual memory effect tends to cause an increase in the amplitude of the annual cycle and a negative effect tends to cause a decrease in amplitude.

[33] The occurrence of a positive diennial memory effect in the felled catchment has the effect of diminishing the amplitude of the annual cycle and, as such, has the same effect as the negative annual memory effect observed in this catchment. The fact that both memory effects would have the same consequence might suggest, they are caused by similar mechanisms. However, as shown above, these two memory effects do not correlate with each other over the period of the record. The increased export of nitrate during periods of high nitrate production would also mean increased transfer into longer residence time storage, e.g., shallow groundwater. Transfer to storage would enhance export at a later data. Decrease in rainfall would lead to decrease in the amount of recharge to the regolith (on the order of a few meters depth) and hence a diminished memory effect at this scale. Evidence for such lag effects has been previously described in the water yield studies at Coweeta [*Douglass and Swank*, 1972]. Changes in the ecosystem resulting from clear-felling and/or natural succession would have little or no effect on these pathways.

[34] The change in the nature and scale of the annual memory effect can now be explained. The change in the annual response represents change in the balance between the hydrological pathways and the reservoirs of available nitrogen. After the catchment is clear-felled, the balance is entirely disrupted and the catchment switches, the annual effect mimicking the diennial effect. This suggests that during this period the entire catchment response, both the diennial and annual effects, are under hydrological pathway limitation. So the release of new reserves of nitrogen that occur as the catchment is clear-felled means that the system in no longer supply-limited but appears to become transport limited. Detailed studies of the N-cycle in the control and felled catchment provide insight into biological responses to clear-felling. Soil organic matter and nitrogen pools increased 20–70% immediately following cutting and logging [*Waide et al.*, 1988]. Increases of 20–250% in mineral nitrogen pools were also observed. These increases in available mineral nitrogen were attributed to moderate increases in measured mineralization and substantial increases in nitrification rates, reductions in soil heterotrophic activity and plant nitrogen uptake, and increases in both symbiotic and free-living N-fixation [*Waide et al.*, 1988]. However, hydrological pathway limitation is linked to ecological succession, specifically the die-back of the major nitrogen fixing species black locust (*Robinia pseudoacacia*), which alters the nature of the nitrogen reservoirs and returns the catchment to something more akin to its initial state. Clear-felling causes the release of nitrogen reserves and results in the disappearance of the negative memory effect, whereas the die-back of black locust gives the reverse effect. It may be initially thought that predation of black locust would create an additional source of nitrogen. However, as one component of the ecosystem dies back another rises to take its place, so as one source is created, i.e., the black locust, the change in succession creates another possible sink. Thus it may be the balance of nitrogen supply across this successional transition rather than just the creation of a new source that causes the observed change in the annual memory effect. An additional component by this stage in the forest regrowth is nitrogen from the decomposition of the woody residues after logging and incorporation in the soil.

[35] Assessing the timescales of the effects suggests that both the clear-felling and the change due to succession are fast transitions. From the argument in the previous section, the transition following clear-felling results in a state that is stable for at least five years and the effect of clear-felling does not diminish over this period. Equally, once there is a return to a negative memory effect that too is relatively stable. The implication being that the annual response is bistable over this period and flips between differing states. Clear-felling of a catchment is a massive intervention and so it is perhaps not surprising that it causes the nature of the catchment response to change, and to change radically. It is nevertheless surprising that this effect does not diminish as the forest ecosystem reestablishes over a period of approximately 12 years after the catchment is clear-felled. Reversion of the memory effect is only caused by the die-back of the major nitrogen fixing species in the catchment (i.e., black locust). This suggests that the change in memory is robust, that the difference between hydrological and nitrogen reservoir limitation is significant, and that the memory of the system will not readily return to a predisturbed state.

[36] The nonlinearity represented by the transition between states in the annual response for the felled catchment can be contrasted with the diennial effect which shows a linear response to changes in temperature but a nonlinear response to changes in rainfall. As observed in the control catchment the memory effect does not correlate with changes in annual rainfall, it only responds once the annual rainfall has decreased dramatically. This could be interpreted as a threshold-type response in catchment behavior and a threshold of rainfall could then be estimated. Equally, the control could be due to changes in the timing of rainfall through the year rather than in its absolute amount; it is not possible to discern which is true in this case. The linearity of the response to changes in temperature may be due to the different timescales between changes in average temperature and changes in rainfall. Long-term changes with the same wavelength as the length of the period of observation, may elicit a more linear response as the catchment has time to adjust.

[37] Prior to clear-felling both catchments 2 and 7, showed no significant impulsivity. The felled catchment develops an impulsive response over the period of observation, but not directly in response to clear-felling. The catchment moves from one stable state, as illustrated by the

control catchment, to a different one as seen after 1989 (Figure 13). Over the same period, the levels of nitrate export from the catchment have increased by an order of magnitude, an increase ascribed to the onset of N-saturation [*Swank and Vose*, 1997]. In a catchment where saturation means that surplus nitrogen is available then it is not surprising that the nitrogen export becomes impulsive with respect to the flow. The onset of stable impulsivity could be taken as indicative of catchment N-saturation. The presence of significant, stable impulsivity after in 1989 suggests that peaks in nitrate would occur coincident with individual storm events, while prior to this time, the impulsivity suggests that decreases in nitrate concentration could occur during storm events.

[38] Taking a systems approach to understanding catchment behavior [*Chorley and Kennedy*, 1971], it is possible to interpret the transition between two states of the annual response as a condition of metastable equilibrium existing between the hydrological flow paths and the nitrogen reserves. This may also be true for the catchment response to rainfall, where the memory effect shows nonlinear, threshold-type behavior. The drought conditions experienced during the period of observation are short-lived on the timescale of the whole record and switches to a drought response can be readily reversed because the rainfall returns in subsequent years. Alternatively, the catchment response is in dynamic equilibrium with respect to temperature changes. However, the nature of change in the catchment response with respect to climatic drivers, metastable vs. dynamic, may correlate more with the typical wavelengths of those drivers, i.e., long-term drivers give a dynamic response while short-term drivers give a metastable response. With respect to ecological succession, the catchment shows a metastable equilibrium with one particular aspect of the succession. Such successional changes are effectively irreversible and represent a thermodynamic trajectory in the catchment response. Changes in this trajectory can be interrupted only by energetic interventions such as clear-felling. The development of impulsivity within the felled catchment with the onset of N-saturation would also appear to represent a thermodynamic trajectory however, N-saturation conditions at this stage in the catchment's regrowth are driven by the nitrogen surplus generated by the felling operations and in the postfelling changes. This supply of nitrogen would be expected to become exhausted as the forest matures and as net primary production remains high, nitrate export would be expected to return to levels similar to that in the control catchment.

5. Conclusions

[39] This study shows that time series analysis represents a useful technique in understanding the integrated response of catchments to internal and external driving forces. Using autoregressive (AR) modeling it is possible to show the existence of significant memory effects. Both catchments show an annual memory effect, but in one catchment this has a positive effect whereas it is a negative effect in the other. In addition, the clear-felled catchment shows a diennial memory effect. These memory effects represent a balance between control by hydrological pathways and control by nitrogen reservoirs, which occur even between neighboring catchments.

[40] The annual memory effect in the control catchment responds to drought conditions while in the felled catchment it reflects the change in vegetation. The diennial month effect in the felled catchment responds to drought conditions independent of the annual effect and of logging operations. Deriving an impulse function for nitrate export with respect to streamflow shows that a significant impulse function develops subsequent to logging. Such a development correlates with the onset of N-saturation within the felled catchment and can be taken as indicative of it. Applying a systems approach shows that the catchment is in metastable equilibrium with respect to its flow paths and nitrogen reserves as influenced by ecological succession and management practice. Similarly, the catchment shows a nonlinear response to changes in rainfall, but is in dynamic equilibrium with temperature changes, reflecting the wavelength of climatic variations over the period of observation. Ecological succession following clear-cutting represents a thermodynamic trajectory, which can only be reset by massive management intervention such as further clear-felling.

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T. P. Burt, Department of Geography, Science Laboratories, South Road, DH1 3LE Durham, UK.

W. T. Swank, Coweeta Hydrologic Laboratory, Southern Research Station, USDA Forest Service, Otto, NC 28763, USA.

F. Worrall, Department of Geological Sciences, Science Laboratories, South Road, DH1 3LE Durham, UK. (fred.worrall@durham.ac.uk)