Time series analysis of the world’s longest fluvial nitrate record: evidence for changing states of catchment saturation

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ABSTRACT

Processes that drive the occurrence of nitrate concentrations in surface waters are known to operate over many decades longer than the available observations. This study considers the world’s longest water quality record of nitrate concentrations in the River Thames (1868 – 2009) in order to understand whether the nature of the time series has changed with time and such external drivers as climate change, land-use of hydrology. The study considers the linear trend, the seasonality, the memory and the impulsivity relative to river flow of the time series for moving windows of 6 years in length. The study can show that:

i) Time series analysis proved effective at discriminating controls upon the nitrate concentration in the long term as different components of the record respond to different drivers in different ways.

ii) There was decoupling of the annual minimum, annual maximum and the amplitude of the seasonal cycle.

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iii) The nature of the time series is dominantly controlled by changes in source of nitrate and not by climate change.

iv) That even similar increases in nitrate concentration in surface waters can have distinct character that illustrates they are the result of different sources of nitrate.

v) Changes in the impulsivity of the record show that the study catchment has recovered from a state of saturation but the memory effect shows that there is an increased contribution from a shallow groundwater.

Keywords: saturation; impulsivity; seasonality, land-use change

INTRODUCTION

When compared to pre-industrial levels, Galloway et al. (2004) has suggested that rate at which biologically-available nitrogen has entered the terrestrial biosphere has doubled as a result of human activity. An increased supply of nitrogen into the terrestrial biosphere has led to, among other things: loss of habitat; lower drinking water quality; lower dissolved oxygen levels; and increased occurrence of algal blooms (Turner and Rabalais, 1994; Vitousek et al., 1997, Burt et al., 2010a,b). In Great Britain, Stuart et al. (2007) have shown that nitrate concentrations in English groundwater have risen by an average of 1 mg N/l/yr since 1990. Equally, the average river nitrate concentration across England and Wales has continued to rise since 1980 with a significant average annual rise of 0.02 mg N/l/yr (unpublished data from DEFRA – www.defra.gov.uk). Furthermore, Worrall et al. (2009a) have shown that the flux of nitrate from Great Britain has increased to 758 ktonnes N/yr (3.3 tonnes N/km²/yr) and has risen significantly since 1974 at an average annual rate of 5.4 ktonnes N/yr. A perspective on the nitrate problem could be gained from the
examination of long-term monitoring records of concentration in surface and
groundwaters. Limbrick (2003) has been able to construct groundwater records of
nitrate concentration from 1904 and although the record is not continuous, it does
provide a baseline against which to judge records from 1974 onwards. Cun and
Vilagines (1997) were able to construct a 90 year long record of annual average
nitrate for the River Seine and showed a step increase in nitrate concentrations in the
mid-1970s. Burt et al. (2008) were able to consider 60-year continuous record of
nitrate concentration river water but from a groundwater-dominated catchment and
showed that the concentration time series represented a breakthrough curve that rose
sharply to a peak in 1980 and has declined since. In this long term context the success
of nitrate management measures can be considered, and indeed, in this context nitrate
sensitive areas and nitrate vulnerable zones (Silgram et al., 2005) cannot yet be
judged as successful; rather the nitrate concentrations in the catchment are responding
to land use changes decades before. Indeed, Worrall et al. (2009b) have shown by use
of time series and comparison with pre- and parallel controls that nitrate vulnerable
zones have yet to be successful even 19 years after their inception. Detailed time
series have also been used to understand processes controlling nitrate release both in
terms of the drivers and internal cycling (Worrall and Burt, 1999). Burt and Worrall
(2009) considered a 35 year long record of stream nitrate concentration in a river and
showed by detailed time series analysis that the long term memory in the series
switches from negative to positive and impulsivity against rainfall becomes
insignificant after a step change and a breakthrough curve. For nitrate release from
soils several studies have shown that time constants for release can be of the order of
40 years (Addiscott, 1988; Whitmore et al., 1992) and so time series shorter than
several decades will hinder interpretation of the processes controlling nitrate
occurrence. Howden et al. (2010) have now compiled the World’s longest water quality record which is for stream water nitrate concentrations. The time series for the nitrate concentration on the River Thames goes back to 1868 and covers not only a period of ongoing climate change and population growth in the catchment, but also a period of massive land use change as a result of forced agricultural change during World War II. Such a long time series allows us to consider whether the nature and not just the magnitude of nitrate concentrations is changing in response to climatic, land use or hydrological factors.

**APPROACH & METHODOLOGY**

*Study site and time series*

The River Thames is the second largest river basin in the UK with a catchment area of 9948 km² at the Kingston gauging station in south west London, close to the tidal limit at Teddington (Figure 1). There are two important aquifers in the basin: the Cretaceous Chalk and the Jurassic limestones: the former is the major water supply to London. Clay vales with extensive modern drainage dominate the area between the two aquifers. The catchment considered lies largely upstream of London but the catchment is still 16% urban with centres at Swindon, Oxford and Reading and over 3 million people living in the catchment by 2010. About 8% of the basin is woodland.

The river nitrate concentration record comprises monthly average nitrate concentrations measured at Hampton between 1868 and 2008 (see Howden et al., 2010, 2011b, 2013).

Nitrate concentration data was listed in archives of the various companies that supplied drinking water to London between 1868 and 2008. Over the 140 years, samples of raw Thames water were taken each weekday and summarized as monthly
averages. In the late 19th century, there were five companies abstracting raw water and, therefore, there are five replicates for each monthly average; these show broad agreement, and were independently verified (Hamlin, 1990). From 1979 to 2008 the monthly averages were calculated from weekly samples. Changes in analytical methods occurred between 1868 and 2008, but none of these caused inhomogeneity in the nitrate record: the observed shifts in concentration modelled here did not coincide with changes in measurement technique.

The great advantage of the Thames catchment is that, not only have there been very long periods of water quality monitoring, but there are also extensive records of the potential driver variables. The following records were available:

Flow records – daily flow records were available from the Teddington monitoring site from mid-1882.

Land-use records – annual agricultural census returns were compiled for each English parish since 1868 until 1989. In 1989 the UK government moved to annual, national-scale reporting with reporting for supra-parish units in 1990, 1995 and 1999. From the year 2000 to present, the UK government has returned to reporting annually but only for supra-parish units. Data from parishes and supra-parish units were combined in order to get the land use of the catchment. It was also possible to consider livestock numbers (overwhelmingly sheep and cattle) over the same period and using the same techniques to give an annual time series of livestock numbers in the catchment. In order to get a consistent livestock record it is assumed that 1 cow = 3.1 sheep (Johnes, 1996), and therefore livestock numbers are expressed as equivalent sheep (sheep_{eq}).

The annual agricultural census does not cover woodland areas and so the area of woodland, including all forestry types, both commercial and semi-natural, was taken from statistics held by the Forestry Commission (Forestry Commission, 2007).
for the years 1924, 1947, 1965, 1980, 1990, 1998 – 2002 and 2008. In order to estimate the area of woodland in the Thames catchment the national trend was rescaled to the area of the Thames catchment not already considered as agricultural land. The area of urban land in the catchment was then considered as the area left unaccounted for by agricultural land or forestry.

In addition to land use it is also possible to estimate the inorganic fertiliser inputs to that land. The Fertiliser Manufacturers Association and the Environment Agency of England and Wales have published annual surveys of the use of synthetic inorganic fertilisers in the UK since 1962 (British Survey of Fertiliser Practice, 2007). Fertiliser use in the UK rose steadily from 1962 to a peak in 1987. For the period before 1962, nitrogen fertiliser inputs were estimated using data from Mittikalli and Richards (1996). Mittikalli and Richards (1996) reported data for “arable” and “grassland” in 1943, 1950, 1957 and 1962, this study used linear interpolation to estimate values for intermediate years. For values before 1943 it was assumed that synthetic fertilizer inputs declined linearly until they were equivalent to the N input from manure (25 kg N/ha/yr). To convert the national-scale values of annual total fertiliser to inputs for the study catchment the recommended values from the UK Fertiliser Best Practice manual (British Survey of Fertiliser Practice, 2007) were used to scale the total annual fertiliser use for any individual year to the average that would be applied for each land-use type for each year in the study catchment.

Climate – detailed rainfall and temperature records have been maintained at Oxford since the 18th century (Burt and Shahgedanova, 1999). Therefore, across the period of water quality monitoring it was possible to give a time series of annual average temperature, and total rainfall.
Time series analysis

The approach to time series analysis taken by this study is that of Worrall and Burt (1998) whereby any time series can be treated as a series of interpretable components – the trend, the seasonal variation and the residual (Eqn 1 – Worrall and Burt, 1998). An additive model can be used where the time series shows no non-stationarity, i.e. there is no interaction between the components over time (Figure 2).

\[ Y(t) = \text{trend} + \text{seasonal variation} + \text{residual} \] (1)

where \( Y(t) \) is the concentration over time. The residual was analysed by autoregressive (AR) modeling.

Time series decomposition

The trend component of the time series was removed by first calculating the best-fit trend line through the time series using the seasonal Kendall test (Hirsch et al., 1982). The seasonal Kendall test was used to assess the significance of any trend and used to estimate the slope of any trend expressed as median annual change in the nitrate concentration. The seasonal Kendall test does not require the underlying dataset to be normally distributed and for the time series in this study there was no need for the inclusion of covariates within the trend analysis (Esterby, 1997).

The seasonal variation was removed by use of seasonal indices of Worrall and Burt (1998). The seasonal indexing approach calculates a median response for the given time step over a pre-defined cycle – in the case of this time series months in the year. The calculated medians for each time step across the seasonal cycle are corrected so that their mean is 1 to give seasonal indices. The seasonal indices
approach is more responsive to the actual data and brings fewer assumptions to the
data than fitting simple harmonic functions derived from Fourier analysis.

Derivation of AR models

Significant AR models were derived using the Mann-Wald process (Mann and Wald, 1943). An AR model was initially calculated for the entire monthly record for $p \leq 15$ in order to identify possible significant AR models. 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 and the fit of the model was checked using the Quenouille method (Quenouille, 1947). The advantage of this approach is that the order of the model can represent both lags in response and memory effects in the time series. Positive and negative memory effects at both six and twelve month time steps have been identified by Worrall and Burt (1999) and hence $p \leq 15$ was used to ensure that annual effects were captured.

Once significant memory effects had been identified from the analysis of the whole sequence, the magnitude of these identified lag effects were followed across the whole time series using a shifting window approach (Worrall et al., 2003). In a shifting window approach the AR(p) model of the selected order (or lag) is calculated over a portion of the time series with a fixed length. Worrall and Burt (1999) suggested that on monthly sampled data a period of 72 months was short enough to give differentiation along the entire series but long enough to find significant effects in a river water nitrate concentration time series. The shifting window approach was applied from the start of the record with the window being shifted by the length of the annual cycle before recalculation of the AR(p) model fit, i.e. overlapping periods were considered. The advantage of using a shifting window approach with
overlapping windows is that transient effects on an inter-annual scale can be examined.

A number of alternative approaches may well produce models with a better fit to the data. Time series models including an allowance for conditional heteroscedasticity (ARCH – Bollersley, 1986) would probably give better predictive power. In the approach to time series analysis taken in this study heteroscedasticity has been assumed as the goal of this research has not been to produce the best-fit to the data for future prediction of water quality but rather to assess and test the response of water quality to internal and external drivers. Equally, one aim of the study is to consider the temporal variation in the whole record, and so therefore use of a non-linear filter (e.g. Kalman filter) would be inappropriate.

Derivation of the impulse function

Transfer-function noise models (TFN) were calculated for the nitrate concentration against the stream-flow 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 was derived as above using the method of Shumway (1988) with flow record decomposed in same manner as the nitrate concentration record. Because the nitrate concentration 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.

The autocorrelation function (ACF) and the partial autocorrelation function (PACF) of the residuals from the decomposition of the time series were examined so as to identify the order of the ARMA model. In a stationary series the number of significant lags in the PACF was taken as an estimate of the order of the autoregressive
component and the ACF was used to estimate the order of the moving average component of the ARMA model. The need for seasonal autoregressive or seasonal moving average component within the ARMA model can also be judged from the PACF and ACF respectively. The variance of the residuals from the estimated ARMA model was used as a measure of model fit and the sufficiency of the fit of the estimated ARMA model was tested by systematically varying the order of the AR and MA components.

The best-fit ARMA model of the input series, i.e. the flow record, was used to filter the output series, i.e. the nitrate concentration record, with the order and coefficients transferred directly from one model to use with the nitrate record. The residuals of fitting the ARMA model to both flow and nitrate time series were cross-correlated with the residuals of the flow record taken as the input and the residuals of the nitrate concentration time series as the response. The resulting cross-correlation function was the impulse function. By removing or the explicable elements of a times the impulse function derived by this approach represents a measure of how responsive the output is to the input, for example, how event-driven is the nitrate concentration record? This approach assumes there is casual feedback between the flow and nitrate records and that the input and output series are independent of each other. The significance of the cross-correlations was tested using a t-test. Again a shifting window approach was used to track changes across the record from the start of consistent riverflow monitoring, i.e. from the first full year of stream gauging in 1883. Gurnell et al. (1992) has described the approach taken here to comparing an input and an out time series creates a reliable and unbiased measure of the relationship without problems of autocorrelation between the two time series.
RESULTS

Trend analysis

The estimated trends in the time windows varied from -0.04 to 0.06 mg N/l/yr, but of the 103 separate time windows where a trend analysis could be performed 63 had no significant trend highlighting the step nature of the time series and the distribution of trends reflects the fact that the step changes were increases and not decreases. The proportion of the variance explained by detrending the data varied from 0 to 75%.

Seasonality

The time series of the month of maximum monthly average nitrate concentration was viewed relative to the water year (month 1 = October) rather than calendar year so that changes between early and later winter were then continuous. The results show that for the first 50 to 60 years of the record the maximum was in the late winter (January to March – Figure 3) but as the influences of the changes in 1939 and WWII start then this maximum comes into early winter and comes as early as October for the 1941 time windows, but the maximum soon shifted back to being in January though it never again stayed as stable in the late winter period again. Conversely, the minimum in the annual cycle did not show such shifts in response to the events of WWII but showed a significant trend in the month in the water year in which the annual minimum occurs with the annual minimum coming earlier in the year (Figure 4). The difference in the time series between that for the minimum and the maximum suggests they are decoupled and under different controls while the minimum appears to respond to a linear driver the maximum does not change linearly but rather shows more abrupt changes. Climate change across the period of the record was a linear and certainly does not show the abrupt changes that are observed in land use, i.e. the
interpretation might be that the annual minimum was controlled by climate while the 
annual maximum respond to changes in sources of nitrate.

The amplitude of the seasonal cycle was assessed as the difference between 
the maximum and minimum monthly indices of the calculated seasonal cycles. The 
amplitude showed a sharp change over the time course of monitoring (Figure 5). Prior 
to the mid-1960s the amplitude of the seasonal cycle varied between 0.5 and 1.87 but 
for the 1968 time window this pattern was broken and for the next 30 years (to the 
1998 time window) the amplitude of the seasonal cycle stayed above 1.87. It is 
possible that the seasonal cycle does respond to the ploughing up in 1939, but that 
disturbance is no different from that which caused a peak in amplitude in 1955 time 
window. Although there are three obvious step changes visible in Figure 2 (between 
1888 and 1898; between 1940 and 1950; and between 1968 and 1978), it now clear 
that they have distinct natures, the latter caused a change in amplitude that the middle 
of the three step changes did not.

**AR modelling**

In attempt to understand the pattern of significant AR components a scree plot was 
considered and showed that after AR(3) there was no change in the number of 
windows showing a significant effect at that order of AR (Figure 6). By far the most 
important of the lags examined in the AR modelling was that at AR(1). The variation 
in the AR(1) coefficient varies from 0 (5 time windows out of 104 shows no 
significant effect) to the highest coefficient 0.95 (Figure 7) the variation in the first 
lag memory effect showed peaks in the 1945 and 1976 time windows and minima in 
1914 time window and between the time windows of 1988 and 1992, i.e. the peaks in 
one month memory effect are the times of the maxima in the two step changes
recorded in the original time series (Figure 2). In all cases at AR(1) the memory effect was positive. Positive memory effects are normally interpreted as storage effects, i.e. a high value of nitrate in one month causes a high value of river water nitrate concentration in the subsequent month because high nitrate water enters shallow groundwater pathways and emerges over the subsequent months to add nitrate to the runoff in the current month. Significant negative memory effects do exist in time series and tracking these across the series shows that no significant negative memory effects were found before AR(2) and by AR(10) all the significant AR effects (16 out of 104 time windows) were negative. Negative memory effects are associated either with exhaustion or dilution due to bypass. At the lags beyond 6 months it was most likely to be an exhaustion effect. However, it is difficult to see any pattern in the series of time windows that show negative AR(p) for lags greater than 6 months. After the removal of the best-fit AR(1) model the proportion of variance explained varies from 21 to 99% with the fit of the model peaking in 1945 and in 1969 i.e. at times of the maximum in the observed step changes.

**Impulse function**

For no time window considered in this study was there a significant impulse effect relative to flow for any lag greater than zero. Conversely, for over half the time windows considered in this study (57 out of 102) there was a significant impulsivity effect relative to flow at the zero lag. For 40 of the windows that showed a significant effect the impulsivity is significantly negative, i.e. an unusually high total flow in one month leads to an unusually low average nitrate concentration in that same month or an unusually low total flow in one month would result in an unusually high average nitrate concentration. That is a significant negative impulsivity at zero lag represents
dilution because the unusually high flow is going via surface pathways that bypass the reserve of available, mobile nitrate. The time windows with significant negative impulsivity fall into two distinct periods. The first one runs between 1903 and 1937, i.e. this period ends with the large scale changes that occur with the onset of WWII (Figure 2). The next period of consecutive time windows was after the 1995 time window. If significant negative impulsivity represents dilution because of the lack of available nitrate in surface pathways then a period when no impulsivity exists means that all flow pathways were equal with respect to available nitrate. The re-occurrence of a significant negative impulsivity in 1995 means that available nitrate in the catchment is decreasing if only in the immediate runoff pathways.

There were 17 time windows where there was a significant positive impulsivity at zero lag with respect to river flow. The only period where there was a sustained period of positive impulsivities was from 1971 through to 1974, i.e. the period that includes the 1976 drought but not the period of high flows after 1980. A positive impulsivity implies that there was high nitrate concentration available in flow pathways only operating at the higher flows.

**DISCUSSION**

The study has highlighted that differing components of the time series respond to different drivers and that there are dramatic changes in nature of the time series that may help aid the interpretation of how changes in environmental drivers are altering the flux of nitrogen through a catchment.

The trend in nitrate concentration across the times series reflects the step changes observed in Figure 2, i.e. occasional large positive trends with a few periods of slow decline. The seasonal cycle however shows a complex response. The annual
minimum shows a linear trend over the period that does not appear to respond to the
major changes in land use or the step changes in nitrate flow observed in the time
series. It was unclear from this record what component of long term climate change
the annual minimum was responding to but it could be rainfall minima or maximum
temperature shifting to earlier in the year. But the annual maximum shifted in
response to land use change and especially into the early period of the large scale land
use change occurring at the beginning of WWII but appears to be short-lived as it
peaks in the period beginning 1941 and by period beginning 1949 the maximum was
back to a position similar to that before the land use change in 1939 – this means a
maximum period of influence of 9 years (1939-1948). It is important to note that this
shift in the annual maximum was not observed at the time of the largest step change in
nitrate concentration in the stream water in the late 1960s. The change after 1939
would be distinct from that in the late 1960s because increases in the immediate
period of WWII would be due to mineralisation of soil organic matter while in the
later step change the source of the nitrate would be artificial fertilisers and
breakthrough from the WWII ploughing up of grassland. Release from mineralisation
would be at its highest when the soils are warmest in late summer and have its
greatest effect as recharge is occurring. This would still be the case for nitrate from
fertiliser but not for nitrate breaking through with the groundwater and so the second
step change in the 1960s is distinct in its source for the earlier step change.

In contrast to the time series of the annual maximum the time series of the
amplitude shows a response to the step change in the late 1960s but not to step change
at the outset of WWII. The step change in the late 1960s has been associated with the
increase in the use of artificial fertilisers and the breakthrough of high nitrate
groundwater. The change in amplitude is both the decline in the annual minimum and
the increase in the annual maximum and this effect stops in 1998. It is difficult to understand how increases in the supply of nitrate to surface water would cause a decline in the annual minimum. However, it might best to remember that the seasonality as calculated by this study is relative to the median and so it is possible that the calculated amplitude can go up without the annual minimum actually decreasing. Examining the actual peak and minimum value in each year of the time series (Figure 2) shows that once the step change occurs the minimum does not actually decline it only declines relative to the median nitrate concentration. This 30 year effect could represent the pulse of the high nitrate groundwater moving through and out of the groundwater system in the catchment. Howden et al. (2011) have measured a 35 year travel time for a nitrate pulses through a chalk aquifer in southern England, although not in the Thames catchment.

With regard to the memory effects within the time series this record was unusual in that it shows very few time periods where there was an annual or semi-annual memory. Worrall et al. (1999) and Worrall et al. (2003) have observed significant annual memory effects that can be interpreted as differences due to wet-dry year differences. For this time series only the 1939 period showed a significant positive annual memory effect. Positive memory effects are associated with a transport-limited situation where there is no shortage of nitrate supply through the catchment flowpaths. However, while the majority of time windows examined showed strong positive one month memory effects, there were no time windows where there was a significant negative one month memory effect. At its peak the one-month memory effect was explaining 95% of the variance in the decomposed times series, i.e. at the height of the step changes observed in the time series the monthly stream concentration was being dominated by a groundwater contribution. There were
periods when the groundwater contribution was at minimum. It is interesting to note
that the last such minimum in the AR(1) effect was between 1988 and 1992, i.e.
groundwater contribution has increased since then even if there has been an apparent
decline in average monthly nitrate concentration.

If the AR modelling shows a period where groundwater flowpaths of typically
1 month residence time were making a large contribution then the impulse function
analysis confirms that there was a period when all flow pathways, surface and
groundwater, were all equal with respect to mobile nitrate. One could think of this
period as one in which the catchment is saturated with respect to nitrate as no matter
which pathway was conducting flow the nitrate was not changing. This period of
saturation comes to an end in mid-1990s not to dissimilar to the period when the
seasonality drastically diminished in importance. The changes in impulsivity do not
distinguish between the two step changes observed in the nitrate time series
suggesting that the relative saturation occurred as a result of the first step change, i.e.
as a result of WWII.

What then can this study then conclude about the nature of this time series?
The study helps confirm the hypothesis of the differing nature of the two step changes
observed in original time series. The time series analysis also shows that the series
was dominated by changes in the source of the nitrate and not by changes driven by
climatic changes. Further it does suggest that the catchment is recovering from the
land use changes in the 1940s and 1960s through the 70s but that there is evidence
that groundwater contribution is increasing as a proportion of declining levels of
nitrate in the surface waters as the saturation state of surface and runoff-dominated
pathways declines and as the one month memory effect increases. Wang et al. (2012)
have considered the travel time of peak nitrate concentrations through UK aquifers
and conclude that although the peak has arrived in many places this has not occurred yet for 60% of chalk aquifers in UK. The result of Wang et al. (2012) does support the result here that groundwater contribution could be increasingly important. Does this study present methods that could be applied elsewhere in order to understand other time series and the nature of the fluvial nitrate pollution? The application of time series analysis to this long and detailed record shows that the step increases observed have a distinct and different character and can be related to differing sources of the nitrate and it was time series analysis that was able to distinguish these patterns. Furthermore, the time series analysis was able to show when the catchment began to recover from high nitrate concentrations and how that was coming about.

CONCLUSIONS

The study has applied a range of time series analysis techniques to the world’s longest water quality record and has shown that:

i) The time series analysis was able to explain up to 99% of the variation in the original time series for periods of 6 years at a time.

ii) That the seasonality of the record was dominated by changes in sources of nitrate, although the annual minimum is controlled by climate change the annual maximum and the amplitude of the seasonal cycle were controlled by the contribution from groundwater.

iii) The memory effect within record shows variations in the contribution of short residence time pathways that peak during the periods of maximum change in nitrate sources and also illustrates that groundwater contribution is again increasing in this catchment.
iv) The impulsivity of the record shows that the catchment saturated with respect to nitrate between WWII and 1995. The analysis shows that most components of the time series were responding to changes in sources and pathways of nitrate rather than to climate change. Furthermore, the study shows the power of time series in highlighting changes in the nature of nitrate pollution rather than just investigating its magnitude.

REFERENCES


Figure 1. Location of the monitoring point within the study catchment.

Figure 2. The time series of monthly average nitrate concentration at Teddington.

Figure 3. The month of the annual maximum in the water year over the course of the time series (1= January to 12= December).

Figure 4. The month of the annual minimum in the water year over the course of the time series.

Figure 5. The amplitude of the seasonal cycle over the course of the time series.

Figure 6. The scree plot of the number of time windows showing significant AR(p) coefficients.

Figure 7. The magnitude in AR(1) coefficient over the course of the time series, values given as zero are those found not to be significant at the 95% probability.

Figure 8. The magnitude in zero lag impulse coefficient relative to riverflow over the course of the time series, values given as zero are those found not to be significant at the 95% probability.