

## Durham Research Online

---

### Deposited in DRO:

28 October 2014

### Version of attached file:

Accepted Version

### Peer-review status of attached file:

Peer-reviewed

### Citation for published item:

Worrall, F. and Howden, N.J.K. and Burt, T.P. (2014) 'Time series analysis of the world's longest fluvial nitrate record : evidence for changing states of catchment saturation.', *Hydrological processes.*, 22 (3). pp. 434-444.

### Further information on publisher's website:

<http://dx.doi.org/10.1002/hyp.10164>

### Publisher's copyright statement:

This is the accepted version of the following article: Worrall, F., Howden, N. J. K. and Burt, T. P. (2014), Time series analysis of the world's longest fluvial nitrate record: evidence for changing states of catchment saturation. *Hydrological Processes*, 29 (3): 434-444, which has been published in final form at <http://dx.doi.org/10.1002/hyp.10164>. This article may be used for non-commercial purposes in accordance With Wiley Terms and Conditions for self-archiving.

### Additional information:

## Use policy

---

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full DRO policy](#) for further details.

1 **Time series analysis of the world's longest fluvial nitrate record: evidence for**  
2 **changing states of catchment saturation**

3

4 Fred Worrall<sup>1</sup>, Nicholas J.K. Howden<sup>2</sup>, and Tim P.Burt<sup>3</sup>.

5 1. Dept of Earth Sciences, Science Laboratories, South Road, Durham, DH1  
6 3LE, UK.

7 2. Dept. of Civil Engineering, University of Bristol, Queens Building, Bristol

8 3. Dept. of Geography, Science Laboratories, South Road, Durham, DH1 3LE,  
9 UK.

10

11 **ABSTRACT**

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

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

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

---

<sup>1</sup> Corresponding author: [Fred.Worrall@durham.ac.uk](mailto:Fred.Worrall@durham.ac.uk); tel no. +44 (0)191 334 2295; fax no. +44 (0)191 334 2301.

- 25 iii) The nature of the time series is dominantly controlled by changes in source of  
26 nitrate and not by climate change.
- 27 iv) That even similar increases in nitrate concentration in surface waters can have  
28 distinct character that illustrates they are the result of different sources of nitrate.
- 29 v) Changes in the impulsivity of the record show that the study catchment has  
30 recovered from a state of saturation but the memory effect shows that there is an  
31 increased contribution from a shallow groundwater.

32

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

34

## 35 **INTRODUCTION**

36 When compared to pre-industrial levels, Galloway et al. (2004) has suggested that rate  
37 at which biologically-available nitrogen has entered the terrestrial biosphere has  
38 doubled as a result of human activity. An increased supply of nitrogen into the  
39 terrestrial biosphere has led to, among other things: loss of habitat; lower drinking  
40 water quality; lower dissolved oxygen levels; and increased occurrence of algal  
41 blooms (Turner and Rabalais, 1994; Vitousek et al., 1997, Burt et al., 2010a,b). In  
42 Great Britain, Stuart et al. (2007) have shown that nitrate concentrations in English  
43 groundwater have risen by an average of 1 mg N/l/yr since 1990. Equally, the average  
44 river nitrate concentration across England and Wales has continued to rise since 1980  
45 with a significant average annual rise of 0.02 mg N/l/yr (unpublished data from  
46 DEFRA – [www.defra.gov.uk](http://www.defra.gov.uk)). Furthermore, Worrall et al. (2009a) have shown that  
47 the flux of nitrate from Great Britain has increased to 758 ktonnes N/yr (3.3 tonnes  
48 N/km<sup>2</sup>/yr) and has risen significantly since 1974 at an average annual rate of 5.4  
49 ktonnes N/yr. A perspective on the nitrate problem could be gained from the

50 examination of long-term monitoring records of concentration in surface and  
51 groundwaters. Limbrick (2003) has been able to construct groundwater records of  
52 nitrate concentration from 1904 and although the record is not continuous, it does  
53 provide a baseline against which to judge records from 1974 onwards. Cun and  
54 Vilagines (1997) were able to construct a 90 year long record of annual average  
55 nitrate for the River Seine and showed a step increase in nitrate concentrations in the  
56 mid-1970s. Burt et al. (2008) were able to consider 60-year continuous record of  
57 nitrate concentration river water but from a groundwater-dominated catchment and  
58 showed that the concentration time series represented a breakthrough curve that rose  
59 sharply to a peak in 1980 and has declined since. In this long term context the success  
60 of nitrate management measures can be considered, and indeed, in this context nitrate  
61 sensitive areas and nitrate vulnerable zones (Silgram et al., 2005) cannot yet be  
62 judged as successful; rather the nitrate concentrations in the catchment are responding  
63 to land use changes decades before. Indeed, Worrall et al. (2009b) have shown by use  
64 of time series and comparison with pre- and parallel controls that nitrate vulnerable  
65 zones have yet to be successful even 19 years after their inception. Detailed time  
66 series have also been used to understand processes controlling nitrate release both in  
67 terms of the drivers and internal cycling (Worrall and Burt, 1999). Burt and Worrall  
68 (2009) considered a 35 year long record of stream nitrate concentration in a river and  
69 showed by detailed time series analysis that the long term memory in the series  
70 switches from negative to positive and impulsivity against rainfall becomes  
71 insignificant after a step change and a breakthrough curve. For nitrate release from  
72 soils several studies have shown that time constants for release can be of the order of  
73 40 years (Addiscott, 1988; Whitmore et al., 1992) and so time series shorter than  
74 several decades will hinder interpretation of the processes controlling nitrate

75 occurrence. Howden et al. (2010) have now compiled the World's longest water  
76 quality record which is for stream water nitrate concentrations. The time series for the  
77 nitrate concentration on the River Thames goes back to 1868 and covers not only a  
78 period of ongoing climate change and population growth in the catchment, but also a  
79 period of massive land use change as a result of forced agricultural change during  
80 World War II. Such a long time series allows us to consider whether the nature and  
81 not just the magnitude of nitrate concentrations is changing in response to climatic,  
82 land use or hydrological factors.

83

## 84 **APPROACH & METHODOLOGY**

### 85 *Study site and time series*

86 The River Thames is the second largest river basin in the UK with a catchment area of  
87 9948 km<sup>2</sup> at the Kingston gauging station in south west London, close to the tidal  
88 limit at Teddington (Figure 1). There are two important aquifers in the basin: the  
89 Cretaceous Chalk and the Jurassic limestones: the former is the major water supply to  
90 London. Clay vales with extensive modern drainage dominate the area between the  
91 two aquifers. The catchment considered lies largely upstream of London but the  
92 catchment is still 16% urban with centres at Swindon, Oxford and Reading and over 3  
93 million people living in the catchment by 2010. About 8% of the basin is woodland.

94 The river nitrate concentration record comprises monthly average nitrate  
95 concentrations measured at Hampton between 1868 and 2008 (see Howden et al.,  
96 2010, 2011b, 2013).

97 Nitrate concentration data was listed in archives of the various companies that  
98 supplied drinking water to London between 1868 and 2008. Over the 140 years, sam-  
99 ples of raw Thames water were taken each weekday and summarized as monthly

100 averages. In the late 19th century, there were five companies abstracting raw water  
101 and, therefore, there are five replicates for each monthly average; these show broad  
102 agreement, and were independently verified (Hamlin, 1990). From 1979 to 2008 the  
103 monthly averages were calculated from weekly samples. Changes in analytical  
104 methods occurred between 1868 and 2008, but none of these caused inhomogeneity in  
105 the nitrate record: the observed shifts in concentration modelled here did not coincide  
106 with changes in measurement technique.

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

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

112 Land-use records – annual agricultural census returns were compiled for each English  
113 parish since 1868 until 1989. In 1989 the UK government moved to annual, national-  
114 scale reporting with reporting for supra-parish units in 1990, 1995 and 1999. From the  
115 year 2000 to present, the UK government has returned to reporting annually but only  
116 for supra-parish units. Data from parishes and supra-parish units were combined in  
117 order to get the land use of the catchment. It was also possible to consider livestock  
118 numbers (overwhelmingly sheep and cattle) over the same period and using the same  
119 techniques to give an annual time series of livestock numbers in the catchment. In  
120 order to get a consistent livestock record it is assumed that 1 cow = 3.1 sheep (Johnes,  
121 1996), and therefore livestock numbers are expressed as equivalent sheep (sheep<sub>eq</sub>).

122         The annual agricultural census does not cover woodland areas and so the area  
123 of woodland, including all forestry types, both commercial and semi-natural, was  
124 taken from statistics held by the Forestry Commission (Forestry Commission, 2007)

125 for the years 1924, 1947, 1965, 1980, 1990, 1998 – 2002 and 2008. In order to  
126 estimate the area of woodland in the Thames catchment the national trend was  
127 rescaled to the area of the Thames catchment not already considered as agricultural  
128 land. The area of urban land in the catchment was then considered as the area left  
129 unaccounted for by agricultural land or forestry.

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

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

149

150 *Time series analysis*

151 The approach to time series analysis taken by this study is that of Worrall and Burt  
152 (1998) whereby any time series can be treated as a series of interpretable components  
153 – the trend, the seasonal variation and the residual (Eqn 1 – Worrall and Burt, 1998).  
154 An additive model can be used where the time series shows no non-stationarity, i.e.  
155 there is no interaction between the components over time (Figure 2).

156

157 
$$Y(t) = \text{trend} + \text{seasonal variation} + \text{residual} \quad (1)$$

158

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

161

162 *Time series decomposition*

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

170 The seasonal variation was removed by use of seasonal indices of Worrall and  
171 Burt (1998). The seasonal indexing approach calculates a median response for the  
172 given time step over a pre-defined cycle – in the case of this time series months in the  
173 year. The calculated medians for each time step across the seasonal cycle are  
174 corrected so that their mean is 1 to give seasonal indices. The seasonal indices



175 approach is more responsive to the actual data and brings fewer assumptions to the  
176 data than fitting simple harmonic functions derived from Fourier analysis.

177

### 178 *Derivation of AR models*

179 Significant AR models were derived using the Mann-Wald process (Mann and Wald,  
180 1943). An AR model was initially calculated for the entire monthly record for  $p \leq 15$   
181 in order to identify possible significant AR models. The order of the AR model was  
182 systematically varied using both a step-up and a step-down procedure so as to avoid  
183 local minima in the model fit and the fit of the model was checked using the  
184 Quenouille method (Quenouille, 1947). The advantage of this approach is that the  
185 order of the model can represent both lags in response and memory effects in the time  
186 series. Positive and negative memory effects at both six and twelve month time steps  
187 have been identified by Worrall and Burt (1999) and hence  $p \leq 15$  was used to ensure  
188 that annual effects were captured.

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

200 overlapping windows is that transient effects on an inter-annual scale can be  
201 examined.

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

211

#### 212 *Derivation of the impulse function*

213 Transfer-function noise models (TFN) were calculated for the nitrate concentration  
214 against the stream-flow record. The first stage of calculating the TFN model is to  
215 derive an autoregressive integrated moving average (ARIMA – Box and Jenkins,  
216 1970) model of the input series, in this case the flow record. The model was derived  
217 as above using the method of Shumway (1988) with flow record decomposed in same  
218 manner as the nitrate concentration record. Because the nitrate concentration time  
219 series (the output series) has been decomposed rather than differenced, the input  
220 series was treated similarly and so the model derived was in fact an ARMA model.  
221 The autocorrelation function (ACF) and the partial autocorrelation function (PACF)  
222 of the residuals from the decomposition of the time series were examined so as to  
223 identify the order of the ARMA model. In a stationary series the number of significant  
224 lags in the PACF was taken as an estimate of the order of the autoregressive

225 component and the ACF was used to estimate the order of the moving average  
226 component of the ARMA model. The need for seasonal autoregressive or seasonal  
227 moving average component within the ARMA model can also be judged from the  
228 PACF and ACF respectively. The variance of the residuals from the estimated ARMA  
229 model was used as a measure of model fit and the sufficiency of the fit of the  
230 estimated ARMA model was tested by systematically varying the order of the AR and  
231 MA components.

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

249

250 **RESULTS**

251 *Trend analysis*

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

257

258 *Seasonality*

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

275 interpretation might be that the annual minimum was controlled by climate while the  
276 annual maximum respond to changes in sources of nitrate.

277         The amplitude of the seasonal cycle was assessed as the difference between  
278 the maximum and minimum monthly indices of the calculated seasonal cycles. The  
279 amplitude showed a sharp change over the time course of monitoring (Figure 5). Prior  
280 to the mid-1960s the amplitude of the seasonal cycle varied between 0.5 and 1.87 but  
281 for the 1968 time window this pattern was broken and for the next 30 years (to the  
282 1998 time window) the amplitude of the seasonal cycle stayed above 1.87. It is  
283 possible that the seasonal cycle does respond to the ploughing up in 1939, but that  
284 disturbance is no different from that which caused a peak in amplitude in 1955 time  
285 window. Although there are three obvious step changes visible in Figure 2 (between  
286 1888 and 1898; between 1940 and 1950; and between 1968 and 1978), it now clear  
287 that they have distinct natures, the latter caused a change in amplitude that the middle  
288 of the three step changes did not.

289

### 290 *AR modelling*

291 In attempt to understand the pattern of significant AR components a scree plot was  
292 considered and showed that after AR(3) there was no change in the number of  
293 windows showing a significant effect at that order of AR (Figure 6). By far the most  
294 important of the lags examined in the AR modelling was that at AR(1). The variation  
295 in the AR(1) coefficient varies from 0 (5 time windows out of 104 shows no  
296 significant effect) to the highest coefficient 0.95 (Figure 7) the variation in the first  
297 lag memory effect showed peaks in the 1945 and 1976 time windows and minima in  
298 1914 time window and between the time windows of 1988 and 1992, i.e. the peaks in  
299 one month memory effect are the times of the maxima in the two step changes

300 recorded in the original time series (Figure 2). In all cases at AR(1) the memory effect  
301 was positive. Positive memory effects are normally interpreted as storage effects, i.e.  
302 a high value of nitrate in one month causes a high value of river water nitrate  
303 concentration in the subsequent month because high nitrate water enters shallow  
304 groundwater pathways and emerges over the subsequent months to add nitrate to the  
305 runoff in the current month. Significant negative memory effects do exist in time  
306 series and tracking these across the series shows that no significant negative memory  
307 effects were found before AR(2) and by AR(10) all the significant AR effects (16 out  
308 of 104 time windows) were negative. Negative memory effects are associated either  
309 with exhaustion or dilution due to bypass. At the lags beyond 6 months it was most  
310 likely to be an exhaustion effect. However, it is difficult to see any pattern in the  
311 series of time windows that show negative AR(p) for lags greater than 6 months.  
312 After the removal of the best-fit AR(1) model the proportion of variance explained  
313 varies from 21 to 99% with the fit of the model peaking in 1945 and in 1969 i.e. at  
314 times of the maximum in the observed step changes.

315

### 316 *Impulse function*

317 For no time window considered in this study was there a significant impulse effect  
318 relative to flow for any lag greater than zero. Conversely, for over half the time  
319 windows considered in this study (57 out of 102) there was a significant impulsivity  
320 effect relative to flow at the zero lag. For 40 of the windows that showed a significant  
321 effect the impulsivity is significantly negative, i.e. an unusually high total flow in one  
322 month leads to an unusually low average nitrate concentration in that same month or  
323 an unusually low total flow in one month would result in an unusually high average  
324 nitrate concentration. That is a significant negative impulsivity at zero lag represents

325 dilution because the unusually high flow is going via surface pathways that bypass the  
326 reserve of available, mobile nitrate. The time windows with significant negative  
327 impulsivity fall into two distinct periods. The first one runs between 1903 and 1937,  
328 i.e. this period ends with the large scale changes that occur with the onset of WWII  
329 (Figure 2). The next period of consecutive time windows was after the 1995 time  
330 window. If significant negative impulsivity represents dilution because of the lack of  
331 available nitrate in surface pathways then a period when no impulsivity exists means  
332 that all flow pathways were equal with respect to available nitrate. The re-occurrence  
333 of a significant negative impulsivity in 1995 means that available nitrate in the  
334 catchment is decreasing if only in the immediate runoff pathways.

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

341

## 342 **DISCUSSION**

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

347         The trend in nitrate concentration across the times series reflects the step  
348 changes observed in Figure 2, i.e. occasional large positive trends with a few periods  
349 of slow decline. The seasonal cycle however shows a complex response. The annual

350 minimum shows a linear trend over the period that does not appear to respond to the  
351 major changes in land use or the step changes in nitrate flow observed in the time  
352 series. It was unclear from this record what component of long term climate change  
353 the annual minimum was responding to but it could be rainfall minima or maximum  
354 temperature shifting to earlier in the year. But the annual maximum shifted in  
355 response to land use change and especially into the early period of the large scale land  
356 use change occurring at the beginning of WWII but appears to be short-lived as it  
357 peaks in the period beginning 1941 and by period beginning 1949 the maximum was  
358 back to a position similar to that before the land use change in 1939 – this means a  
359 maximum period of influence of 9 years (1939-1948). It is important to note that this  
360 shift in the annual maximum was not observed at the time of the largest step change in  
361 nitrate concentration in the stream water in the late 1960s. The change after 1939  
362 would be distinct from that in the late 1960s because increases in the immediate  
363 period of WWII would be due to mineralisation of soil organic matter while in the  
364 later step change the source of the nitrate would be artificial fertilisers and  
365 breakthrough from the WWII ploughing up of grassland. Release from mineralisation  
366 would be at its highest when the soils are warmest in late summer and have its  
367 greatest effect as recharge is occurring. This would still be the case for nitrate from  
368 fertiliser but not for nitrate breaking through with the groundwater and so the second  
369 step change in the 1960s is distinct in its source for the earlier step change.

370 In contrast to the time series of the annual maximum the time series of the  
371 amplitude shows a response to the step change in the late 1960s but not to step change  
372 at the outset of WWII. The step change in the late 1960s has been associated with the  
373 increase in the use of artificial fertilisers and the breakthrough of high nitrate  
374 groundwater. The change in amplitude is both the decline in the annual minimum and



375 the increase in the annual maximum and this effect stops in 1998. It is difficult to  
376 understand how increases in the supply of nitrate to surface water would cause a  
377 decline in the annual minimum. However, it might best to remember that the  
378 seasonality as calculated by this study is relative to the median and so it is possible  
379 that the calculated amplitude can go up without the annual minimum actually  
380 decreasing. Examining the actual peak and minimum value in each year of the time  
381 series (Figure 2) shows that once the step change occurs the minimum does not  
382 actually decline it only declines relative to the median nitrate concentration. This 30  
383 year effect could represent the pulse of the high nitrate groundwater moving through  
384 and out of the groundwater system in the catchment. Howden et al. (2011) have  
385 measured a 35 year travel time for a nitrate pulses through a chalk aquifer in southern  
386 England, although not in the Thames catchment,

387         With regard to the memory effects within the time series this record was  
388 unusual in that it shows very few time periods where there was an annual or semi-  
389 annual memory. Worrall et al. (1999) and Worrall et al. (2003) have observed  
390 significant annual memory effects that can be interpreted as differences due to wet-  
391 dry year differences. For this time series only the 1939 period showed a significant  
392 positive annual memory effect. Positive memory effects are associated with a  
393 transport-limited situation where there is no shortage of nitrate supply through the  
394 catchment flowpaths. However, while the majority of time windows examined  
395 showed strong positive one month memory effects, there were no time windows  
396 where there was a significant negative one month memory effect. At its peak the one-  
397 month memory effect was explaining 95% of the variance in the decomposed times  
398 series, i.e. at the height of the step changes observed in the time series the monthly  
399 stream concentration was being dominated by a groundwater contribution. There were

400 periods when the groundwater contribution was at minimum. It is interesting to note  
401 that the last such minimum in the AR(1) effect was between 1988 and 1992, i.e.  
402 groundwater contribution has increased since then even if there has been an apparent  
403 decline in average monthly nitrate concentration.

404         If the AR modelling shows a period where groundwater flowpaths of typically  
405 1 month residence time were making a large contribution then the impulse function  
406 analysis confirms that there was a period when all flow pathways, surface and  
407 groundwater, were all equal with respect to mobile nitrate. One could think of this  
408 period as one in which the catchment is saturated with respect to nitrate as no matter  
409 which pathway was conducting flow the nitrate was not changing. This period of  
410 saturation comes to an end in mid-1990s not too dissimilar to the period when the  
411 seasonality drastically diminished in importance. The changes in impulsivity do not  
412 distinguish between the two step changes observed in the nitrate time series  
413 suggesting that the relative saturation occurred as a result of the first step change, i.e.  
414 as a result of WWII.

415         What then can this study then conclude about the nature of this time series?  
416 The study helps confirm the hypothesis of the differing nature of the two step changes  
417 observed in original time series. The time series analysis also shows that the series  
418 was dominated by changes in the source of the nitrate and not by changes driven by  
419 climatic changes. Further it does suggest that the catchment is recovering from the  
420 land use changes in the 1940s and 1960s through the 70s but that there is evidence  
421 that groundwater contribution is increasing as a proportion of declining levels of  
422 nitrate in the surface waters as the saturation state of surface and runoff-dominated  
423 pathways declines and as the one month memory effect increases. Wang et al. (2012)  
424 have considered the travel time of peak nitrate concentrations through UK aquifers

425 and conclude that although the peak has arrived in many places this has not occurred  
426 yet for 60% of chalk aquifers in UK. The result of Wang et al. (2012) does support the  
427 result here that groundwater contribution could be increasingly important.

428 Does this study present methods that could be applied elsewhere in order to  
429 understand other time series and the nature of the fluvial nitrate pollution? The  
430 application of time series analysis to this long and detailed record shows that the step  
431 increases observed have a distinct and different character and can be related to  
432 differing sources of the nitrate and it was time series analysis that was able to  
433 distinguish these patterns. Furthermore, the time series analysis was able to show  
434 when the catchment began to recover from high nitrate concentrations and how that  
435 was coming about.

436

## 437 **CONCLUSIONS**

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

- 440 i) The time series analysis was able to explain upto 99% of the variation in the  
441 original time series for periods of 6 years at a time.
- 442 ii) That the seasonality of the record was dominated by changes in sources of  
443 nitrate, although the annual minimum is controlled by climate change the  
444 annual maximum and the amplitude of the seasonal cycle were controlled by  
445 the contribution from groundwater.
- 446 iii) The memory effect within record shows variations in the contribution of short  
447 residence time pathways that peak during the periods of maximum change in  
448 nitrate sources and also illustrates that groundwater contribution is again  
449 increasing in this catchment.

450 iv) The impulsivity of the record shows that the catchment saturated with respect  
451 to nitrate between WWII and 1995.

452 The analysis shows that most components of the time series were responding to  
453 changes in sources and pathways of nitrate rather than to climate change.  
454 Furthermore, the study shows the power of time series in highlighting changes in  
455 the nature of nitrate pollution rather than just investigating its magnitude.

456

## 457 **REFERENCES**

458 Addiscott, T.M. (1988). Long-term leakage of nitrate from bare unmanured soil. *Soil*  
459 *Use and Management* 4, 91-95.

460 Bollersley, T. (1986). Generalized autoregressive conditional heteroskedasticity.  
461 *Journal of Econometrics* 31, 307-327.

462 Box, G.E.P., and G.M.Jenkins (1970). Time-series Analysis: forecasting and control.  
463 Holden-Day, San Francisco.

464 British Survey of Fertiliser Practice (2007). Fertiliser use on farm crops for crop year  
465 2006. HMSO, London.

466 Burt, T.P., and M.Shahgedanova (1999). An historical record of evaporation losses  
467 since 1815 calculated using long-term observations from the Radcliffe  
468 Meteorological Station, Oxford, England. *Journal of Hydrology* 205, 1-2 , 101-  
469 111.

470 Burt, T.P., N. J. K. Howden, F. Worrall, and M. J. Whelan (2008). Importance of  
471 long-term monitoring for detecting environmental change: lessons from a  
472 lowland river in south east England. *Biogeosciences* 5, 1529 -1535.

473 Burt, T.P. and F. Worrall. (2009). Stream nitrate levels in a small catchment in south  
474 west England over a period of 35 years (1970-2005). *Hydrological Processes* 23,  
475 14, 2056-2068.

476 Burt, T. P., N. J. K. Howden, F. Worrall, M. J. Whelan, and M. Z. Bieroza (2011a),  
477 Nitrate in the United Kingdom Rivers: Policy and its outcomes since 1970,  
478 *Environ. Sci. Technol.*, 45, 175–181, doi:10.1021/es101395s.

479 Burt, T. P., N. J. K. Howden, F. Worrall, and J J. McDonnell (2011b), On the value of  
480 long-term, low-frequency water quality sampling: Avoiding throwing the baby  
481 out with the bathwater, *Hydrol. Processes*, 25(5), 828–830,  
482 doi:10.1002/hyp.7961.

483 Cun, C., and R. Vilagines (1997). Time series analysis on chlorides, nitrates,  
484 ammonium and dissolved oxygen concentrations in the Seine river near Paris.  
485 *The Science of the Total Environment* 208, 1, 59-69.

486 Esterby, S.R. (1997). Review of methods for detection and estimation of trends with  
487 emphasis on water quality applications. in *Water quality trends and geochemical*  
488 *mass balance*, edited by N.E.Peters, O.P.Bricker, and M.M.Kennedy, pp. 3-26,  
489 John Wiley and Sons, Chichester, UK.

490 Forestry Commission (2007). *Forestry facts and figures*. The Forestry Commission,  
491 Edinburgh.

492 Galloway, J.N., F.J. Dentener, D.G. Capone, E.W. Boyer, R.W. Howarth, S.P.  
493 Seitzinger, G.P. Asner, C.C. Cleveland, P.A. Green, E.A. Holland, D.M. Karl,  
494 A.E. Michaels, J.H. Porter, A.E. Townsend, and C.J. Vorosmarty (2004).  
495 Nitrogen cycles: past, present and future. *Biogeochemistry* 70, 153-226.

496 Gurnell, A.M., M.J.Clar and C.T.Hill (1992). Analysis and interpretation of patterns  
497 within and between hydroclimatological time series in an alpine glacier basin.  
498 *Earth Surface Process and Landforms* 17: 821-839.

499 Hamlin, C. (1990), *A Science of Impurity: Water Analysis in Nineteenth Century*  
500 *Britain*, 346 pp., Adam Hilger, Bristol, U. K.Hirsch, R.M., J.R.Slack and  
501 R.A.Smith (1982). Techniques of trend analysis for monthly water quality data.  
502 *Water Resources Research* 18, 107-121.

503 Howden, N.J.K., T.P.Burt, F.Worrall, and M.J.Whelan (2010). Nitrate concentrations  
504 and fluxes in the River Thames over 140 years (1868 to 2008): are increases  
505 irreversible?. *Hydrological Processes* 24, 18, 2657-2662.

506 Howden, N.J.K., T.P.Burt, S.A.Mathias, F.Worrall, M.J.Whelan, and M.Bieroza  
507 (2011a). Modelling long-term diffuse nitrate pollution at the catchment-scale:  
508 data, parameter and epistemic uncertainty. *Journal of Hydrology* 403, 3-4, 337-  
509 351.

510 Howden, N.J.K., T. P. Burt, F. Worrall, S. Mathias, and M. J. Whelan (2011b),  
511 Nitrate pollution in intensively farmed regions: What are the prospects for  
512 sustaining high-quality groundwater?, *Water Resour. Res.*, 47, W00L02,  
513 doi:10.1029/ 2011WR010843.

514 Howden, N.J.K, TP Burt, F Worrall , SA Mathias & MJ Whelan (2013): Farming for  
515 Water Quality: Balancing Food Security and Nitrate Pollution in UK River  
516 Basins, *Annals of the Association of American Geographers*, 103:2, 397-407,  
517 <http://dx.doi.org/10.1080/00045608.2013.754672>

518 Johnes, P.J. (1996). Evaluation and management of the impact of land use change on  
519 the nitrogen and phosphorus load delivered to surface waters: The export  
520 coefficient modelling approach. *Journal of Hydrology* 183, 323-349.

521 Limbrick, K.J., (2003). Baseline nitrate concentrations in groundwater of the chalk in  
522 south Devon, UK. *Science of the Total Environment* 314, 89-98.

523 Mann, H.B., and A.Wald (1943). On the treatment of linear stochastic difference  
524 equations. *Econometrica* 11, 173-220.

525 Mittikalli, N.M., and K.S.Richards (1996). Estimation of Surface Water Quality  
526 Changes in Response to Land Use Change: Application of The Export  
527 Coefficient Model Using Remote Sensing and Geographical Information System.  
528 *Journal of Environmental Management* 48, 263–282.

529 Quenouille, M.H. (1947). A large-sample of autoregressive schemes. *J. Royal*  
530 *Statistical Society* 110, 123-129.

531 Shumway, R.H. (1988). Applied statistical time series analysis. Prentice Hall,  
532 London.

533 Silgram, M., A.Williams, R.Waring, I.Neumann, Hughes A, Mnasour M, Besien T,  
534 (2005). Effectiveness of the nitrate sensitive areas scheme in reducing  
535 groundwater concentrations in England. *Quarterly Journal of Engineering*  
536 *Geology and Hydrogeology* 38, 117-127.

537 Stuart, M.E., P.J.Chilton, D.G.Kinniburgh, and D.M.Cooper (2007). Screening for  
538 long-term trends in groundwater nitrate monitoring data. *Quarterly Journal of*  
539 *Engineering Geology and Hydrogeology*, 40, 361-376.

540 Turner, R.F., and N.N.Rabalais (1994). Coastal eutrophication near the Mississippi  
541 River delta. *Nature* 368, 619-621.

542 Vitousek, P.M., J.D. Aber, R.W. Howarth, G.F. Likens, P.A. Matson, D.W. Schindler,  
543 W.H. Schlesinger, and D.G. Tilman (1997). Human alteration of the global  
544 nitrogen cycle: sources and consequences. *Ecological Applications* 7, 737-750.

545 Wang, L., M. E. Stuart, J. P. Bloomfield, A. S. Butcher, D. C. Gooddy, A. A.  
546 McKenzie, M. A. Lewis, and A. T. Williams. (2012). Prediction of the arrival of  
547 peak nitrate concentrations at the water table at the regional scale in Great  
548 Britain. *Hydrological Processes* 26, 2, 226-239.

549 Whitmore, A.P., N.J. Bradbury, and P.A. Johnson (1992), Potential contribution of  
550 ploughed grassland to nitrate leaching. *Agriculture, Ecosystems and Environment*  
551 39, 221-233.

552 Worrall, F., and T.P.Burt (1998). Decomposition of river water nitrate time series –  
553 comparing agricultural and urban signals. *Science of the Total Environment*  
554 210/211: 153-162.

555 Worrall, F., and T.P.Burt (1999). A univariate model of river water nitrate time series.  
556 *Journal of Hydrology* 214, 74-90.

557 Worrall, F., W.T.Swank, and T.P.Burt (2003). Changes in nitrate export due to  
558 ecological succession, land management and climate: developing a systems  
559 approach to integrated catchment response. *Water Resources Research* 39, 7, 1-  
560 14.

561 Worrall, F., T.P.Burt, N.J.K.Howden, and M.Whelan (2009a), The Fluvial Flux of  
562 Nitrogen from Great Britain 1974 – 2005 in the context of the terrestrial nitrogen  
563 budget of Great Britain. *Global Biogeochemical Cycles* 23, GB3017.

564 Worrall, F., E.Spencer, and T.P. Burt. (2009b). The effectiveness of nitrate vulnerable  
565 zones for limiting surface water nitrate concentrations. *Journal of Hydrology* 370,  
566 1-4, 21-28.

567

568

569



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

571

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

573

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

576

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

579

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

581

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

584

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

587

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

591

592

593

594