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

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

34

35 INTRODUCTION

When compared to pre-industrial levels, Galloway et al. (2004) has suggested that rate 36 37 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 38 terrestrial biosphere has led to, among other things: loss of habitat; lower drinking 39 water quality; lower dissolved oxygen levels; and increased occurrence of algal 40 blooms (Turner and Rabalais, 1994; Vitousek et al., 1997, Burt et al., 2010a,b). In 41 Great Britain, Stuart et al. (2007) have shown that nitrate concentrations in English 42 groundwater have risen by an average of 1 mg N/l/yr since 1990. Equally, the average 43 44 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 45 DEFRA - www.defra.gov.uk). Furthermore, Worrall et al. (2009a) have shown that 46 the flux of nitrate from Great Britain has increased to 758 ktonnes N/yr (3.3 tonnes 47 N/km²/yr) and has risen significantly since 1974 at an average annual rate of 5.4 48 ktonnes N/yr. A perspective on the nitrate problem could be gained from the 49

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

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

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84 APPROACH & METHODOLOGY

85 Study site and time series

The River Thames is the second largest river basin in the UK with a catchment area of 86 9948 km² at the Kingston gauging station in south west London, close to the tidal 87 limit at Teddington (Figure 1). There are two important aquifers in the basin: the 88 Cretaceous Chalk and the Jurassic limestones: the former is the major water supply to 89 London. Clay vales with extensive modern drainage dominate the area between the 90 two aquifers. The catchment considered lies largely upstream of London but the 91 catchment is still 16% urban with centres at Swindon, Oxford and Reading and over 3 92 93 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.

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:

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

Land-use records – annual agricultural census returns were compiled for each English 112 parish since 1868 until 1989. In 1989 the UK government moved to annual, national-113 scale reporting with reporting for supra-parish units in 1990, 1995 and 1999. From the 114 year 2000 to present, the UK government has returned to reporting annually but only 115 for supra-parish units. Data from parishes and supra-parish units were combined in 116 order to get the land use of the catchment. It was also possible to consider livestock 117 numbers (overwhelmingly sheep and cattle) over the same period and using the same 118 119 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, 120 1996), and therefore livestock numbers are expressed as equivalent sheep (sheep_{eq}). 121

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)

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 130 131 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 132 133 inorganic fertilisers in the UK since1962 (British Survey of Fertiliser Practice, 2007). Fertiliser use in the UK rose steadily from 1962 to a peak in 1987. For the period 134 before 1962, nitrogen fertiliser inputs were estimated using data from Mittikalli and 135 Richards (1996). Mittikalli and Richards (1996) reported data for "arable" and 136 "grassland" in 1943, 1950, 1957 and 1962, this study used linear interpolation to 137 estimate values for intermediate years. For values before 1943 it was assumed that 138 synthetic fertilizer inputs declined linearly until they were equivalent to the N input 139 from manure (25 kg N/ha/yr). To convert the national-scale values of annual total 140 fertiliser to inputs for the study catchment the recommended values from the UK 141 Fertiliser Best Practise manual (British Survey of Fertiliser Practice, 2007) were used 142 to scale the total annual fertiliser use for any individual year to the average that would 143 144 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 18th 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.

150 *Time series analysis*

The approach to time series analysis taken by this study is that of Worrall and Burt 151 (1998) whereby any time series can be treated as a series of interpretable components 152 - the trend, the seasonal variation and the residual (Eqn 1 – Worrall and Burt, 1998). 153 An additive model can be used where the time series shows no non-stationarity, i.e. 154 there is no interaction between the components over time (Figure 2). 155 156 Y(t) = trend + seasonal variation + residual (1) 157 158 where Y(t) is the concentration over time. The residual was analysed by 159 autoregressive (AR) modeling. 160 161 Time series decomposition 162 The trend component of the time series was removed by first calculating the best-fit 163 trend line through the time series using the seasonal Kendall test (Hirsch *et al.*, 1982). 164

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 normality 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 thedata than fitting simple harmonic functions derived from Fourier analysis.

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178 Derivation of AR models

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

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

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 to the data. Time series models including an allowance for conditional 203 heteroscedasticity (ARCH - Bollersley, 1986) would probably give better predictive 204 power. In the approach to time series analysis taken in this study hetereoscedasticity 205 206 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 207 208 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-209 linear filter (e.g. Kalman filter) would be inappropriate. 210

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212 Derivation of the impulse function

Transfer-function noise models (TFN) were calculated for the nitrate concentration 213 against the stream-flow record. The first stage of calculating the TFN model is to 214 derive an autoregressive integrated moving average (ARIMA - Box and Jenkins, 215 1970) model of the input series, in this case the flow record. The model was derived 216 as above using the method of Shumway (1988) with flow record decomposed in same 217 manner as the nitrate concentration record. Because the nitrate concentration time 218 219 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. 220 The autocorrelation function (ACF) and the partial autocorrelation function (PACF) 221 222 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 223 lags in the PACF was taken as an estimate of the order of the autoregressive 224

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 232 233 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 234 residuals of fitting the ARMA model to both flow and nitrate time series were cross-235 correlated with the residuals of the flow record taken as the input and the residuals of 236 the nitrate concentration time series as the response. The resulting cross-correlation 237 function was the impulse function. By removing or the explicable elements of a times 238 the impulse function derived by this approach represents a measure of how responsive 239 the output is to the input, for example, how event-driven is the nitrate concentration 240 record? This approach assumes there is casual feedback between the flow and nitrate 241 records and that the input and output series are independent of each other. The 242 significance of the cross-correlations was tested using a t-test. Again a shifting 243 244 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. 245 Gurnell et al. (1992) has described the approach taken here to comparing an input and 246 an out time series creates a reliable and unbiased measure of the relationship without 247 problems of autocorrelation between the two time series. 248

250 **RESULTS**

251 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%.

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258 Seasonality

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

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

277 The amplitude of the seasonal cycle was assessed as the difference between the maximum and minimum monthly indices of the calculated seasonal cycles. The 278 amplitude showed a sharp change over the time course of monitoring (Figure 5). Prior 279 to the mid-1960s the amplitude of the seasonal cycle varied between 0.5 and 1.87 but 280 281 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 282 283 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 284 window. Although there are three obvious step changes visible in Figure 2 (between 285 1888 and 1898; between 1940 and 1950; and between 1968 and 1978), it now clear 286 that they have distinct natures, the latter caused a change in amplitude that the middle 287 of the three step changes did not. 288

289

290 AR modelling

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

300 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. 301 a high value of nitrate in one month causes a high value of river water nitrate 302 concentration in the subsequent month because high nitrate water enters shallow 303 groundwater pathways and emerges over the subsequent months to add nitrate to the 304 runoff in the current month. Significant negative memory effects do exist in time 305 306 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 307 308 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 309 likely to be an exhaustion effect. However, it is difficult to see any pattern in the 310 series of time windows that show negative AR(p) for lags greater than 6 months. 311 312 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 313 times of the maximum in the observed step changes. 314

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316 Impulse function

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

dilution because the unusually high flow is going via surface pathways that bypass the 325 reserve of available, mobile nitrate. The time windows with significant negative 326 impulsivity fall into two distinct periods. The first one runs between 1903 and 1937, 327 i.e. this period ends with the large scale changes that occur with the onset of WWII 328 (Figure 2). The next period of consecutive time windows was after the 1995 time 329 window. If significant negative impulsivity represents dilution because of the lack of 330 331 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 332 333 of a significant negative impulsivity in 1995 means that available nitrate in the catchment is decreasing if only in the immediate runoff pathways. 334

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 impulsitivty implies that there was high nitrate concentration available in flow pathways only operating at the higher flows.

341

342 **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

350 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 351 352 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 353 temperature shifting to earlier in the year. But the annual maximum shifted in 354 response to land use change and especially into the early period of the large scale land 355 356 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 357 358 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 359 shift in the annual maximum was not observed at the time of the largest step change in 360 nitrate concentration in the stream water in the late 1960s. The change after 1939 361 would be distinct from that in the late 1960s because increases in the immediate 362 period of WWII would be due to mineralisation of soil organic matter while in the 363 later step change the source of the nitrate would be artificial fertilisers and 364 breakthrough from the WWII ploughing up of grassland. Release from mineralisation 365 would be at its highest when the soils are warmest in late summer and have its 366 greatest effect as recharge is occurring. This would still be the case for nitrate from 367 fertiliser but not for nitrate breaking through with the groundwater and so the second 368 step change in the 1960s is distinct in its source for the earlier step change. 369

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 375 understand how increases in the supply of nitrate to surface water would cause a 376 decline in the annual minimum. However, it might best to remember that the 377 seasonality as calculated by this study is relative to the median and so it is possible 378 that the calculated amplitude can go up without the annual minimum actually 379 decreasing. Examining the actual peak and minimum value in each year of the time 380 381 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 30 382 383 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 384 measured a 35 year travel time for a nitrate pulses through a chalk aquifer in southern 385 England, although not in the Thames catchment, 386

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

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 404 1 month residence time were making a large contribution then the impulse function 405 406 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 407 408 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 409 saturation comes to an end in mid-1990s not to dissimilar to the period when the 410 seasonality drastically diminished in importance. The changes in impulsivity do not 411 412 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. as a result of WWII. 414

415 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 416 observed in original time series. The time series analysis also shows that the series 417 was dominated by changes in the source of the nitrate and not by changes driven by 418 419 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 420 that groundwater contribution is increasing as a proportion of declining levels of 421 nitrate in the surface waters as the saturation state of surface and runoff-dominated 422 pathways declines and as the one month memory effect increases. Wang et al. (2012) 423 have considered the travel time of peak nitrate concentrations through UK aquifers 424

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 428 understand other time series and the nature of the fluvial nitrate pollution? The 429 application of time series analysis to this long and detailed record shows that the step 430 431 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 432 433 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 434 was coming about. 435

436

437 CONCLUSIONS

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

- i) The time series analysis was able to explain upto 99% of the variation in theoriginal time series for periods of 6 years at a time.
- ii) That the seasonaility 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.

450 iv) The impulsivity of the record shows that the catchment saturated with respect451 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.

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570	Figure 1. Location of the monitoring point within the study catchment
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572	Figure 2. The time series of monthly average nitrate concentration at Teddington.
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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).
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577	Figure 4. The month of the annual minimum in the water year over the course of the
578	time series.
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580	Figure 5. The amplitude of the seasonal cycle over the course of the time series.
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582	Figure 6. The scree plot of the number of time windows showing significant AR(p)
583	coefficients.
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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.
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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.
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