

1 **The problem of self-correlation in fluvial flux data – the case of nitrate flux from UK**
2 **rivers**

3
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8
9 **Abstract**

10 This study proposes a general method for testing for self-correlation (also known as spurious
11 or induced correlation) in comparisons where there is a common variable, e.g. the comparison
12 of the fluvial flux of a component with water yield. We considered the case of the fluvial flux
13 of nitrate from 153 catchments from across the UK for which there were at least 10 years of
14 data. The results show that 66% of records (102 catchments) could be rejected as
15 significantly self-correlated ($P < 95\%$). Among the 51 catchments, which proved to be
16 significantly different from the spurious, or self-correlated result, the response was variable
17 with linear, convex, s-curve and mixed results proving the best description. There was no
18 spatial pattern across the UK for the results that were and were not rejected as spurious; the
19 most important predictor of not being self-correlated was the length of record rather than any
20 catchment characteristic. The study shows that biogeochemical stationarity cannot be
21 assumed and that caution should be applied when examining fluvial flux data.

22
23 **Keywords:** spurious correlation; induced correlation; biogeochemical stationarity

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25 **Introduction**

26 Significant correlations can occur in data that are entirely spurious and not related to any
27 causal or physical relationships between the variables being compared (Kenney, 1982). Such
28 spurious correlations (also referred to as induced or self-correlation) will occur where there is
29 common variable in the comparison, e.g. A vs. A/B, A*B vs. B or A/B vs. C/B). The strength
30 of the self-correlation will increase where the variance in the common variable is large in
31 comparison to that of the other or unique variables. Kenney (1982) pointed out that the
32 reverse can also be the case: self-correlation can weaken a strong relationship when the
33 variance of the common variable is equal to or less than that of the other or unique variable.
34 Furthermore, spurious correlation is enhanced whenever log-transformation has been used.
35 Interpretations based upon plots or relationships with common variables are frequently
36 applied and their occurrence has been discussed relative to atmospheric sciences (e.g. Baas et
37 al., 2006); is raised as an issue in geomorphological data (Gani et al., 2007); and the
38 correlations of parts and wholes in ecology (eg. stand biomass and tree measurements – Dean
39 and Cao, 2003).

40 Several studies have proposed methods for identifying spurious correlation. The
41 strength of relationship between two variables can be tested by standard statistical tests of the
42 correlation coefficient. Pearson (1897), in the original study of spurious correlation, gives an
43 approximation of the correlation coefficient that would be expected for the correlation of two
44 variables both ratioed to a third. However, Pearson's formula is only an approximation and so
45 tests based upon randomisation have become more common. McCuen and Surbeck (2008)
46 observed that many environmental models (e.g. Michaelis-Menten kinetics) are calibrated by
47 linearization based upon plots that include a common variable; they recommend avoiding
48 such a linearization step and used non-linear fitting methods but provided no test of spurious
49 correlation. Lenahan et al. (2011) discussed "induced correlations" with respect to

50 hydrochemical data and especially the comparison of ratio data and summed data, and used
51 randomisation to view self-correlation but, they provided no formal account of how
52 randomisation was performed nor how to compare between the observed and the randomised
53 data. Jackson and Somers (1991) placed randomisation tests in the same context as the null
54 hypothesis and therefore stated that, when comparing ratioed variables, the null hypothesis
55 used not that the regression coefficient was zero but rather the null hypothesis was that the
56 regression coefficient was the expected value (usually the arithmetic mean) of the distribution
57 of regression coefficients resulting from randomisation of the data, however, Jackson and
58 Somers (1991) provided no suggestion for making this comparison. Kenney (1982)
59 formulated the self-correlated regression coefficient for normally distributed data in the
60 comparison A+B vs. B and Vickers et al. (2009a) used this approach to consider surface
61 exchange of CO₂; they considered the test to be that the regression coefficient was greater
62 than the value predicted by the formulation of Kenney (1982).

63 There are several problems with these approaches used to assess self-correlation;
64 firstly, some of the above provide no formal test method at all; secondly, the formulations so
65 far provided are either approximations or for specific comparisons; thirdly, many methods
66 provide no formal test of the difference between the randomised results and the observed.
67 Alternatively, we propose a different method and test for the detection of induced correlation.
68 For the randomisation we propose that we do not assume a normal distribution and that other
69 distributions or no distribution at all would be more appropriate for some datasets. The
70 difference between the randomly generated and the observed data will be statistically tested
71 and, furthermore the nature of the best-fit line will be considered relative to the randomised
72 data.

73 Within hydrology, the self-correlation is evident in a number of common approaches
74 to analysing and interpreting data. The authors of this paper have themselves previously used

75 comparisons that we might consider upon reflection to be vulnerable to self-correlation.
76 Worrall et al. (2008) and Worrall and Burt (2008) compared changes in annual DOC flux in a
77 range of catchments over periods of severe droughts to the changes in annual discharge as a
78 means of testing whether there was a biogeochemical response to drought. Worrall et al.
79 (2012) modelled 125 years of Ca flux data by comparing it to annual discharge and, perhaps
80 not surprisingly, annual discharge was the most important factor in explaining the Ca flux.
81 The USEPA (2005) actually recommend using the correlation between pollutant flux and
82 discharge in order to improve flux estimation and Shivers and Moglen (2008) provide an
83 alternative approach on this basis. However, a strong linear relationship between component
84 flux (e.g. nitrate) and annual discharge has been used to suggest biogeochemical stationarity
85 (sometimes also referred to as chemiostasis, eg. Stackpoole et al., 2014) as an emergent
86 property of catchments (Basu et al. 2010). However, Godsey et al. (2009) argued for
87 chemiostasis on the basis of concentration discharge relationships. Basu et al. (2010) use the
88 term biogeochemical stationarity to a low variation in concentration of a component relative
89 to hydrological variation. This biogeochemical stationarity is taken to arise from a legacy of
90 available material present in the catchment that means no matter which pathways water takes
91 through a catchment the results is very similar, i.e. stationary. A strong linear relationship
92 between component flux and discharge (annual water yield) suggests a single concentration
93 of the component exists across a wide range of flows. This test of stationarity has been used
94 for dissolved carbon (Giesler et al., 2014, Jantze et al., 2013).

95 The sediment delivery ratio (SDR) is a common approach used to explain changes in
96 sediment flux through a catchment (Roehl, 1962; Burt and Allison, 2010~~09~~). The SDR
97 approach is vulnerable to self-correlation yet correlations based upon the variation of
98 sediment yield with catchment area are commonly used, interpreted and discussed (e.g.
99 Tetzlaff et al., 2013). Worrall et al. (2014) have shown that such approaches do suffer from

100 self-correlation. In the SDR context, a negative relationship between SDR and catchment area
101 would be predicted and so positive relationships might be thought to be free of self-
102 correlation. Such relationships between SDR and catchment area have been observed in a
103 number of studies (e.g. Church and Slaymaker, 1989).

104 Prairie and Bird (1989) in their defence of part versus whole analysis in biology warn
105 of “not throwing the baby out with the bath water”, an attitude also taken by Francey et al.
106 (2010, 2011) in their analysis of pollution loads. Therefore, in the hope of making the most of
107 the available information this study considers how self-correlated, or spurious correlation,
108 can tested for and how to consider relationships in comparisons vulnerable to spurious
109 correlation.

110

111 **Methods**

112 *Data set*

113 The Harmonised Monitoring Scheme (HMS) was established in 1974 to measure important
114 hydrochemical fluxes to the North Atlantic and to allow their trends to be monitored
115 (Simpson, 1980). These measurements met the UK’s commitment to a series of international
116 agreements and treaties (Bellamy and Wilkinson, 2001): ~~and~~ [standards and consistency of](#)
117 [measurement over time and space are defined within the HMS programme](#). There are 56
118 HMS sites in Scotland and 214 sites in England and Wales. Monitoring sites were placed at
119 the tidal limits of all rivers with an average annual discharge of over $2 \text{ m}^3\text{s}^{-1}$, with additional
120 sites placed on major tributaries. These criteria means that there is good spatial coverage of
121 the coast of England and Wales but in Scotland many of the west coast rivers are too small to
122 warrant inclusion in the HMS. A range of water quality parameters are measured at these
123 sites: pertinent to this study, the HMS measures nitrogen as nitrate and river discharge
124 (instantaneous discharge and daily average discharge).

125 Monitoring is the responsibility of regional offices of the Environment Agency in
126 England and Wales and the Scottish Environment Protection Agency in Scotland. As a result,
127 sampling frequencies vary ranging from sub-weekly to monthly (or even less frequently in
128 some cases). Data from any year at any site where fewer than 12 samples were collected in
129 that year were excluded from the analysis. Consequently, although there are 270 HMS sites
130 across Great Britain, the number of sites which could be included in any one year was
131 variable: the distribution of sites from which data were used is shown in Figure 1.
132 Furthermore, because self-correlation relies on examining a correlation and so only sites with
133 at least 10 years of annual flux data were considered.

134 In addition to the use of data from the HMS sites, this study considered the World's
135 longest water quality record, the Thames at Teddington (Howden et al., 2011). [Howden et al.
136 \(2011\) have demonstrated the consistency and coherence of this record over the 126 years.](#)
137 The record at Teddington consists of monthly average nitrate concentrations since 1867 but
138 river discharge records were only available for complete calendar years from 1883 to 2008 –
139 126 years of data. Therefore, the correlation between annual nitrate flux from the Thames at
140 Teddington and the annual water yield was analysed for self-correlation in the same way as
141 data from the HMS.

142

143 *Flux calculation*

144 For cases where data are relatively sparse, such as in much of the HMS, Littlewood et al.
145 (1998) suggested that the product of flow weighted concentration and the annual discharge
146 was most appropriate. However, HMS sampling is generally aperiodic and the following
147 method (Rodda and Jones, 1983) is more appropriate:

148

$$149 \quad F_{jy} = KA_y \sum_1^N n_y C_i Q_i \quad (i)$$

150
$$n_y = \frac{A_y}{N_y} \quad (\text{ii})$$

151

152 where F_{jy} = the annual flux at the site j for a given year y (tonnes N/yr); C_i = the measured
153 concentration at the site at time i (mg N/l); Q_i = the river discharge at time i (m^3/s); K = a
154 conversion factor which takes into account the units used (0.0864); n_y = average number of
155 days between samples (days); N_y = the number of samples at the site in year y; and A_y = the
156 number of days in year y (can vary with a leap year). This approach assumes that each sample
157 taken at a site is equally likely to be representative of an equal proportion of the year as any
158 other sample.

159 For the purpose of this study no attempt is made to sample bias correct the estimates
160 of nitrate flux or of annual water yield for two reasons. Previous studies that have compared
161 flux vs. yield plots have not sample bias corrected their estimates. Secondly, given the pairing
162 of the data for concentration and flow there would be a sample bias in both that would be of
163 similar order of magnitude which would mean the overall effect may be small.

164

165 ***Estimation of self-correlation***

166 Vickers et al. (2009a) suggested a method for testing the occurrence and magnitude of self-
167 correlation. To apply this method to the problem of comparing flux and annual water yield, a
168 single value of concentration is drawn at random from the normal distribution fitted to the
169 observed concentration data and paired with a value of stream discharge drawn at random
170 from the normal distribution of stream discharge data. The process is repeated to derive the
171 required number of random pairs for calculation of an annual flux and annual water yield (in
172 the case here a number of pairs equal to or greater than 12). The process can be repeated as
173 many times as desired so that sufficient pairs of estimates of annual flux and annual water

174 yield exist and these can be plotted against each other and compared to the observed pairs of
175 annual flux and annual water yield. If there is no significant difference between the best-fit
176 line for the observed data and the best-fit line from the randomised data then any line fitted to
177 the observed data, can be dismissed as spurious due to self-correlation. However, there are
178 several problems with this approach. Firstly, the randomisation process assumes that the data
179 from which the calculation was derived are normally distributed. This situation was true for
180 the gas flux data which Vickers et al. (2009a) studied but this is unlikely to be true for the
181 concentration and stream discharge data that need to be considered here. Therefore, this study
182 considered normal, log normal, and gamma distributions in order to select random pairs of
183 data from the observed concentration and stream discharge. However, the assumption of
184 normality made by Vickers et al. (2009a), or indeed the assumption of any distribution
185 assumes that sufficient data would be available such that a distribution of whatever sort could
186 be accurately fitted. Given that in this study annual flux was calculated based on as few as 12
187 samples per year, fitting complex distributions with repeatable accuracy would be difficult.
188 As an alternative approach, this study selected at random concentration and stream discharge
189 data not from a distribution fitted to the observed but taken at random from each of the
190 actually observed data series. This second approach requires no assumption about the
191 distribution of the data. Thirdly, it was assumed that a straight line relationship exists but that
192 this is not necessarily the case and indeed more complex descriptions of the relationship
193 between flux and annual water yield may be found and so this model considers linear, power
194 law, exponential and sigmoidal relationships (Weibull function). The Aikike Information
195 Criterion (AIC) was used to decide between relationships given the additional degrees of
196 freedom from 2 to 4.

197 For additional comparison the value of the self-correlated regression for normally
198 distributed data was calculated (Kenney, 1982):

199

$$200 \quad r^2 = \frac{1}{\left(1 + \frac{\sigma_{com}}{\sigma_{uni}}\right)} \quad (iii)$$

201

202 Where: σ_{com} = the standard deviation of the common variable (for this study riverflow); σ_{uni} =
203 the standard deviation of the unique variable (for this study nitrate concentration).

204

205 *Catchment characteristics*

206 To help understand the occurrence of self-correlation, the results were compared to a range of
207 catchment properties including soil, land use and hydrological characteristics. The dominant
208 soil of each 1 km² grid square in Great Britain was classified into mineral, organo-mineral
209 and organic soil based upon the classification system of Hodgson (1997); note that by this
210 definition peat soils are a subset of organic soils. The land use for each 1 km² square of Great
211 Britain was classified into: arable, grass and urban based upon the June Agricultural Census
212 for 2004. Note that values for forested land are not available from this census. In addition,
213 the number of cattle and sheep in each cell were counted from the June Agricultural Census
214 for 2004. Catchment areas were calculated from the CEH Wallingford digital terrain model
215 which has a 50 m grid interval and a 0.1 m altitude interval. The soil and land-use
216 characteristics for each 1 km² grid square were summed across catchment areas and
217 expressed as percentages of each catchment area. Within the catchments for which N flux
218 information was available both soil and land-use properties were expressed as percentages of
219 catchment area. For livestock, equivalent sheep per hectare values were calculated based on
220 a ratio of 3.1 sheep per cow (Johnes and Heathwaite, 1997). In addition, it was possible to
221 give a range of hydrological characteristics for each catchment. Based upon data from the
222 National River Flow Archive (www.nrfa.ac.uk), hydroclimatic measures used were: base
223 flow index (BFI; Gustard et al., 1992); average actual evaporation, the average annual

224 rainfall; and by difference the average runoff for each catchment for which flux data were
225 available. Also included in the analysis were: the sample size for each catchment, the ratio of
226 the concentration variance to flow variance for each catchment; and the self-correlation
227 regression coefficient as predicted by Equation (iii).

228 The presence, or absence, of self-correlation was then compared to the catchment
229 characteristics using logistic regression analysis, Logistic regression analysis was fitted to the
230 binary response variable (presence/absence of self-correlation) using maximum likelihood
231 techniques; the fit of the analysis was assessed using correct classification; and importance of
232 variables within any logistic regression was measured using the odds ratio.

233

234 **Results**

235 Across all HMS data from 1974 to 2010, it was possible to assess 105019 pairs of
236 concentration and flow data in 153 catchments (Figure 1) – these catchments ranged in scale
237 from 4 to 9885 km². For the 153 catchments, the median number of years that could be
238 considered was 31, with an inter-quartile range of 24 to 34 years; the minimum number of
239 years at any one site was 12 years. At the 95% probability that the null hypothesis can be
240 rejected, i.e. a 95% probability that the observed data relationship is different from that due to
241 spurious or self-correlation, then 51 out of 153 catchments show a relationship significantly
242 different from the random relationship. 136 catchments had a better than 50% chance of
243 being different from random correlation, leaving 17 catchments with no better than 50%
244 chance of being spuriously correlated. The self-correlated regression coefficient, as predicted
245 by Equation (iii), varied from 0.2 to 0.999; 69 catchments had an $r_{sc}^2 > 0.99$ and the median
246 $r_{sc}^2 = 0.95$, i.e. it would be very difficult using the approach of Kenney (1982) to prove
247 anything other than self-correlated data. The ratio of the concentration variance to the flow
248 variance has a median value 2.6% with an inter-quartile range between 0.2 and 13.6%, i.e. the

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249 calculation is dominated by the flow variance which is the common variable. The spatial
250 distribution of the self-correlation shows no obvious spatial distinction (Figure 2) although
251 two regions showed only self-correlated catchments and they were north Scotland and the
252 Scottish Borders. The region with the lowest proportion of self-correlated catchments was
253 Wales.

254 Within the 51 catchments identified as having a greater than 95% chance of not being
255 self-correlated a range of behaviours were then identified using the AIC to identify the best-
256 fit response. Of the 51, 18 showed a straight line response, 5 showed a curve response, and 3
257 catchments showed a sigmoidal (s-curve) response (Figure 3). For 23 catchments the
258 response would better be described as triangular. The straight line responses (Figure 4) all
259 show a line of significant lower gradient than predicted on the basis of randomisation alone.
260 The curved response (Figure 5) was always convex up in the significant results, i.e. as flow
261 increased the flux decreased and this can be interpreted as dilution at higher flows either due
262 to exhaustion of the nitrate supply or the bypassing of the nitrate reservoir. The s-curve
263 response (Figure 6) could be interpreted as a mixture of sources. The triangular responses
264 appear to be bounded by two trends one of which was very close to the line predicted from
265 randomisation and the other at a lower gradient than that predicted for self-correlation (Figure
266 7). The spatial distribution of the type of response (Figure 3) does suggest a differentiation
267 either side of a north-east to south-west axis with the triangular or mixed response
268 dominating in north west England and Wales while linear and convex up, curved responses
269 dominate in south east England. Such a north west to south east division follows the geology
270 of the UK with younger, more permeable geology dominating in south east England and less
271 permeable, Palaeozoic geology dominating to the north west.

272 The results from the 126 years of record for the Thames show a mixed response in
273 comparison to the results from the HMS records (Figure 7). Firstly, there was no single

274 response for the Thames and by the standards of this study the results must be dismissed as
275 self-correlated; however, this may belie a more complex response. As was observed for many
276 of the catchments in the HMS dataset for many of the years in the Thames record there is a
277 straight line response between flux and yield at values below that predicted from
278 randomisation but the response is also bound by a sigmoidal response above the line
279 predicted by randomisation.

280 Applying logistic regression analysis to the binary response defined by the 95%
281 probability of not being self-correlated showed that the probability of not being self-
282 correlated is best-predicted by:

$$284 \log_e \left(\frac{\theta}{1-\theta} \right) = 2.24 \log_e n + 0.51 \log_e (Area) - 0.39 \log_e (Arable) - 10.4 \quad (iv)$$

$$285 \quad \quad \quad (0.9) \quad \quad (0.25) \quad \quad (0.12) \quad \quad (3.3)$$

286
287 Where θ = the probability that the catchment is not self-correlated; n = the number of years in
288 the record; Area = catchment area (km²); Arable = area of arable land within the catchment
289 (km²); Only characteristics found to be significantly different from zero at the 95%
290 probability were included and the values in the brackets below each term are the standard
291 errors in the coefficient or the constant. Equation (iv) correctly classified 75% of the 153
292 catchments but it should be remembered that, if the equation classified all catchments as
293 being self-correlated, then it would get 67% correct classification. Indeed, Equation (iv)
294 correctly classified 13 out of 51 non-self-correlated catchments. The odds ratio suggests that the
295 most important variable is the length of the record (n) followed by the catchment area (Area).
296 However, the odds ratio for the arable variable is less than 1 suggesting that it is only in
297 combination with the other variables that it is significant

298

299 **Discussion**

300 A number of objections to the idea of self-correlation have been raised. Prairie and Bird
301 (1989) claim that self-correlation for ratio data is not problematic, and will only occur when
302 large measurement errors are present in the variables; that log transformation will reduce
303 spurious correlation; that the variables are meaningful and represent concepts of interest.
304 How the latter is itself spurious as the concept of interest may only have arisen as the result of
305 a spurious correlation and indeed biogeochemical stationarity is a case in point. Lasslop et al.
306 (2009) argued that the case raised by Vickers et al. (2009a) was not a case of spurious
307 correlation given that the component is not part of the derived variable (gross primary
308 production compared to ecosystem respiration), unlike the case where the whole is compared
309 to a part (body weight to liver weight). Vickers et al. (2009b) have refuted the arguments of
310 Lasslop et al. (2009) as irrelevant because self-correlation was demonstrated and that GPP
311 was not measured independently of the ecosystem respiration. Indeed, self-correlated results
312 appear and persist often because they are mechanistically plausible, e.g. one would expect the
313 flux of nitrate to increase with increased annual discharge.

314 With respect to biogeochemical stationarity, Gall et al. (2013) have shown that
315 biogeochemical stationarity to be mechanistically plausible as sources mix and in-stream
316 processes dominate with increasing scale, leading to decreasing influence of the diversity of
317 behaviours in the headwaters. However, given the possible self-correlated nature of the
318 primary evidence of biogeochemical stationarity, then Occam's razor must apply and so the
319 more complex explanation must not be used until self-correlation has been tested for and
320 rejected. However, the evidence ~~from~~ this study of 153 catchments across a range of scales
321 would suggest that even when self-correlation could be rejected, then stationarity is not
322 necessarily the best explanation but rather there may in fact be a range of different
323 explanations.- [Gall et al. \(2013\) predict more biogeochemical stationarity with increase scale](#)

324 and catchment size, however, the reverse was observed in this case. Equation (iv) actually
325 shows that self-correlation was less likely with greater catchment area and self-correlation
326 was less likely if there was not a linear response. This result would suggest that mix of
327 sources becomes more and not less important up to the scales considered by this study, i.e.
328 upto 9885 km².

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329 Although straight line responses were commonly found in this analysis the common
330 response was best described as a mixture of sources with different sources operating at
331 different times of the year or at different flow conditions. Jackson and Somers (1991)
332 reminds us that the real hypothesis test when dealing with comparisons with a common
333 variable is the comparison between the line generated from randomisation and the observed
334 line and not just the existence of a significant relationship. Therefore, given the results above,
335 the observation of straight lines is not only that they are best described as straight lines but
336 also they are all at values lower than the randomised line, i.e. nitrate fluxes might appear
337 lower than would be expected and this could simply be that lower concentrations are more
338 likely to be at higher flows, i.e. in general runoff events dilute the main nitrate source.
339 Indeed, whenever a curve response was found then it was always convex up, i.e. as annual
340 water yield increased there was increased dilution of the nitrate responses. However, the most
341 common result was a triangular one where the data were bounded by two trends. Such a
342 response means that it is possible that for any given annual water yield a range of nitrate
343 fluxes could be possible. An easy explanation of this degeneracy is that over time the
344 catchment has changed in terms of the sources of nitrate to the stream, for example, land use
345 has changed from low input pasture to high-input arable; or perhaps there have been
346 improvements at wastewater treatment works in highly urbanised catchments. ~~the convex up~~
347 results

348 With respect to the prediction of fluxes, use of the self-correlated relationship
349 between flux and yield could ~~be considered to~~ appear to work because, in effect it samples a
350 flux estimate from the distribution of known flux estimates and so therefore it represents a
351 reasonable estimate of the flux, but this estimate could be achieved without reference to
352 annual water yield. Self-correlation might well arise, in these circumstances ~~self-correlation~~
353 ~~may exist~~ because of the sampling frequency. The scatter in the graph of component flux
354 versus annual water yield ~~self-correlation~~ may arise because of limited sampling relative to
355 the nature of the hydrological variation within a monitored catchment and ~~at the~~ such low
356 frequency of sampling, common for the catchments in this study, ~~where~~ a sample could be
357 taken at very similar discharges but in very distinct hydrological contexts, e.g. a sample taken
358 on rising limb versus a sample taken on and recession limb of the storm hydrograph.

359

360 **Conclusions**

361 This study has proposed a general approach to assess self-correlation (spurious or induced
362 correlation) in situations where there is a common variable and conditions of normality do
363 not hold. Application of this method to nitrate fluvial flux data shows that, even for datasets
364 of more than 10 years, self-correlation was found in 66% of the 153 study catchments. Self-
365 correlation was mainly related to length of record with longer records being less likely to be
366 self-correlated. Amongst those records that were not self-correlated, there were a range of
367 behaviours with the most common being a “triangular” behaviour implying a mixing of
368 sources rather than biogeochemical stationarity.

369

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373

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480 Figure 1. The study catchments that could be used within this study.

481

482 Figure 2. The distribution of sites found not to be significantly self-correlated at the 95%
483 probability in comparison to those found to be significantly self-correlated..

484

485 Figure 3. The distribution of the best-fit curve type for those sites which were shown not to
486 be significantly self-correlated.

487

488 Figure 4. Example of a linear response between nitrate flux and annual water yield in
489 comparison to the line predicted from randomized data (---). The catchment is the River
490 Lee at Lee Valley Road.

491

492 Figure 5. Example of a convex up, curve response between nitrate flux and annual water
493 yield in comparison to the line predicted from randomized data. The catchment is the
494 River Lee at Ware Lock.

495

496 Figure 6. Example of an s-curve (ogive) response between nitrate flux and annual water yield
497 in comparison to the line predicted from randomized data. The catchment is the River
498 Severn at Haw Bridge.

499

500 Figure 7. Example of an triangular response between nitrate flux and annual water yield. The
501 response predicted for randomized data is shown (---) in comparison to the other
502 proposed bounding trend. The catchment is the River Conwy at Cwm Llanerch.

503

504 Figure 8. The nitrate flux vs. annual water yield plot for the River Thames in comparison to
505 the line predicted by randomisation.