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Nitrate concentrations and fluxes in the River Thames over 140 years (1868–2008): are increases irreversible?

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Human activity has doubled the loading of biologically available nitrogen to the terrestrial biosphere compared to pre-industrial levels (Vitousek *et al*., 1997; Galloway *et al*., 2004; Schlesinger *et al*., 2006; Seitzinger *et al*., 2006). This has led to a sixfold increase in global fluxes of fluvial dissolved inorganic nitrogen (Green *et al*., 2004) contaminating surface- and groundwater as terrestrial ecosystems become increasingly nitrogen-saturated (Foster *et al*., 1982; Meybeck, 1982; Aber *et al*., 1998; Bouwman *et al*., 2005; Mulholland *et al*., 2008; Ju *et al*., 2009; Qiu, 2009; Worrall *et al*., 2009). Nitrate is one of the most problematic and widespread of water contaminants (Howden and Burt, 2008, 2009): it has been regulated on the basis of its alleged toxicity to humans (Sandor *et al*., 2001; Addiscott and Benjamin, 2004), but elevated fluvial nitrate concentrations and fluxes are detrimental to both river and marine ecology (Burt *et al*., 1993). Nitrate originates from land-based, diffuse (spatially distributed) agricultural sources due to land management (e.g. fertilizer application; Goolsby and Battaglin, 2001) or changes in land use (e.g. long-term release of soil nitrogen (N) resulting from ploughing of permanent grassland; Whitmore *et al*., 1992), and from discharges of sewage effluent direct to rivers (Howden *et al*., 2009). Inputs may also occur from nitrogen fixation in the soil, atmospheric deposition and bedrock weathering (Holloway *et al*., 1998). It is essential that we understand the mechanisms controlling the movement of nitrate through river basins to the oceans, such that likely impacts on river ecology, potable water supply and marine tropic status may be identified. A key and poorly understood component is identification of the timescales over which river basin-scale nitrate transport occurs. This is of interest because modelling studies (Young *et al*., 1976; DOE, 1986; Howden and Burt, 2008) have suggested that changes in land use could be responsible for elevated mean fluvial concentrations persisting for some decades after initial land use change.

Some of the earliest water quality measurements ever made were for water treatment works abstracting London's water supply from the River Thames (Meybeck, 2005); systematic and independently verifiable data are available from 1868 (Hamlin, 1990). Here, we present a continuous monthly record of average nitrate concentrations for the Thames at Hampton (just upstream of London) for 140 years starting in 1868 (Figure 1), the longest continuous record of water chemistry available anywhere in the world (*cf* Raymond *et al*., 2008). Nitrate concentrations rose during World War II (WWII) and then stabilized at almost double their previous level ($\sim$2 mg/l 1868–1940, $\sim$4 mg/l 1945–1970). There was a further step change in the early 1970s, when the average concentrations jumped from around 4 mg/l to almost 8 mg/l and, in common with the WWII increase, these concentrations have remained stubbornly high despite continent-wide interventions to reduce catchment nitrogen inputs since the early 1980s (EU Nitrates Directive 91/676). Such shifts in concentration may be driven by changes in the climate, flow regime, land use or population. Figure 2 shows

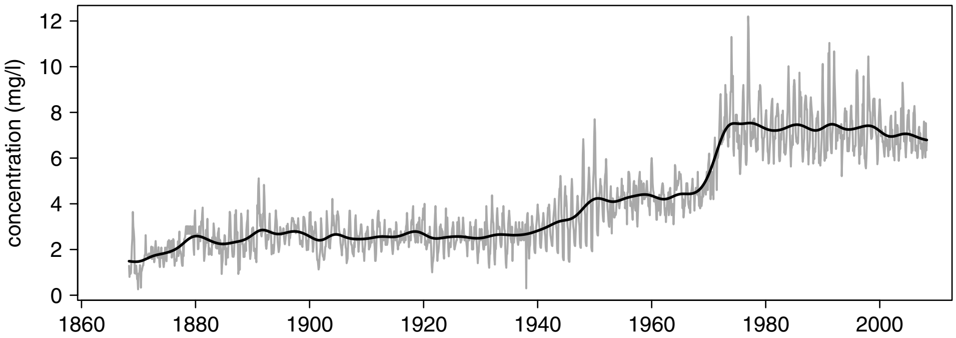

Figure 1. Time series plot of monthly nitrate concentration (mg NO_3–N/l), with an approximate 1-year moving average (Watson, 1966)

monthly precipitation and average temperatures for the Thames Basin, but neither of these is associated with observed changes in nitrate concentration. Furthermore, although the Thames Basin population has increased steadily over the last 140 years, there have been no abrupt changes in basin population in the mid-1940s or early 1970s that could explain the shifts as a nitrate contribution from sudden increases in sewage effluent (Figure 2). Therefore, these concentration changes must have resulted from changes in flow regime or land use.

We used river discharge data, available at the same site for 125 years (1884–2008), to calculate fluvial nitrate fluxes. There are three ways to increase nitrate flux: increase the river discharge, increase the nitrate concentration or a combination of both. An increase in nitrate concentration without a change in discharge results in an increased nitrate export for the same discharge. Changes in the export–discharge relationship may be detected by normalizing fluxes to the rate of discharge (Raymond *et al.*, 2008). We do this by calculating the nitrate flux at an average discharge F_{avD}. This is shown in Figure 3, which indicates three different flux–discharge relationships. The first is evident for water years (WYs) from 1884 to 1945 (period 1), the second for WYs from 1946 to 1971 (period 2) and the third for WYs from 1972 to 2008 (period 3). The flux–discharge relationships were approximated by linear regression on log transformed data using

$$\log[F] = \log[a] + b\log[Q] \tag{1}$$

leading to the untransformed $F_{avD} - Q$ relationship

$$F_{avD} = aQ^b \tag{2}$$

with parameter b being the same for all three periods and a for periods 1, 2 and 3 being 0·141, 0·257 and 0·382, respectively. We tested for homogeneity of slopes between the three regressions, finding no significant interactions between independent variable and period ($p > 0{\cdot}647$ and $p > 0{\cdot}914$ comparing period 1 with periods 2 and 3, respectively), but did find significant differences in a for all three ($p < 2\text{e}{-16}$ for all parameters). This suggests that the only significant change to the $F_{avD} - Q$ relationship is an increase in a

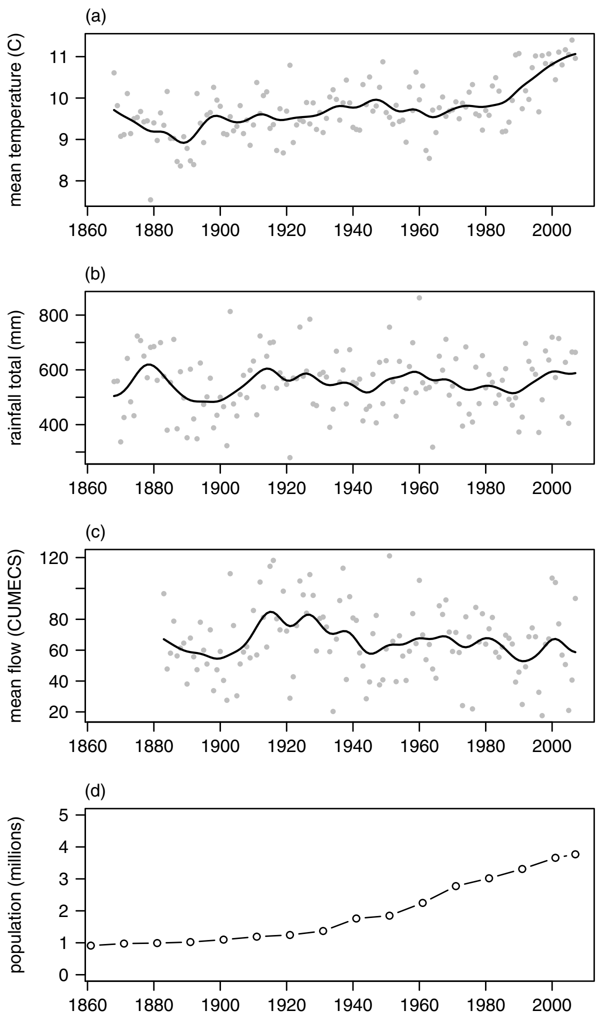

Figure 2. Time series plots of annual (a) average temperature (°C); (b) rainfall total (mm); (c) river discharge (m^3/s). For each time series individual monthly values are plotted. The lines plot an approximate decadal moving average (Watson, 1966). Monthly rainfall totals and average temperatures are from the Radcliffe Observatory, Oxford, in the centre of the Thames Basin, continuous for the period of record (from May 1868 to September 2008); flow data are taken from the Teddington Weir at Kingston (1883–2008); (d) population taken from decadal census data, 1861–2001

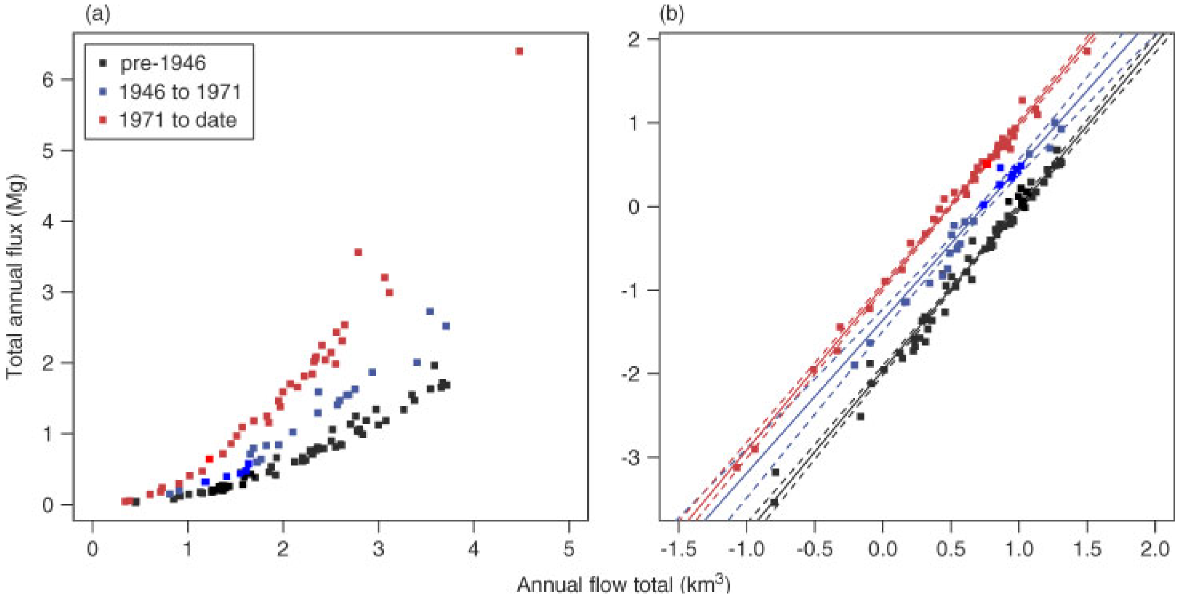

Figure 3. Nitrate–nitrogen (NO_3–N) flux-discharge relationships for water years (WYs) 1884–2008. For 1884–1945 the parameters are $a = -1{\cdot}95810$ ($\pm 0{\cdot}02832$) and $b = 1{\cdot}95056$ ($\pm 0{\cdot}0351$) ($r^2 = 0{\cdot}9804$, $p < 2{\cdot}2e{-}16$); for 1946–1971 the parameters are $a = -1{\cdot}35846$ ($\pm 0{\cdot}06445$) and $b = 1{\cdot}82965$ ($\pm 0{\cdot}08429$)($r^2 = 0{\cdot}9476$, $-<2{\cdot}2e{-}16$); and for 1972–2008 the parameters are $a = -0{\cdot}96196$ ($\pm 0{\cdot}02212$) and $b = 1{\cdot}95139$ ($\pm 0{\cdot}02809$) ($r^2 = 0{\cdot}993$, $-<2{\cdot}2e{-}16$)

which, for the equivalent average discharge, increases F_{avD} in the ratio 1 : 1·82 : 2.71 for periods 1, 2 and 3, respectively. We checked for changes in hydrological drivers that may have contributed to the observed shift in the$F_{avD} - Q$ relationship, but an analysis of covariance (ANCOVA) of the precipitation–discharge (P–Q) relationship showed no significant difference between the three periods, with homogeneity of slopes confirmed by a lack of interaction between period and independent variable ($p > 0{\cdot}317$ and $p > 0{\cdot}478$ comparing period 1 with periods 2 and 3, respectively). It is most striking that the big shifts in the $F_{avD} - Q$ relationship are unidirectional: the data show fluxes either increasing or remaining stable. There is no evidence of any decrease, despite large-scale intervention to limit nitrogen inputs.

Land use change is the only basin-wide driver that can account for the shifts in concentration shown in Figure 1. Figure 4 shows the fraction of the Thames Basin under arable crops and the estimated total nitrate input to the catchment system. By far the most sudden changes were during WWII and in the mid-1960s; these are reflected in the nitrate record shortly after. The immediate increase represents near-stream and shallow subsurface runoff sources in parts of the catchment, whereas the sustained shift in mean concentration reflects long-residence time groundwater pathways (Jackson *et al.*, 2006; 2008; Howden and Burt, 2008). Differences in the relative magnitudes of the two-step changes can be explained as follows. The extensive wartime ploughing of permanent grassland was achieved through mechanization, but there is no evidence of increased fertilizer application (Stamp, 1948). In the 1960s, a smaller area of grassland was converted to arable but this was accompanied by increases in the grant-aided land drainage (Green, 1979) and considerable intensification, especially a substantial increase in fertilizer application: annual fertilizer use in the UK was 485 kt N in 1960, increasing to 921 kt N by 1970 and peaking at 1588 kt N in 1984. The second shift in concentration is more rapid because increased under drainage reduced catchment residence time and because inorganic fertilizers are immediately available for leaching. Reversions from arable to grassland are not reflected in the nitrate record and concentrations remain obstinately high after each increase. Since the early 1980s, attempts to manage high nitrate concentrations have focused on control of nitrogen fertilizer inputs. While fertilizer input is certainly a contributing factor to rising nitrate concentrations, the stepped increases are driven by longer-term processes following land use change: release of soil N and groundwater transport both operate on at least decadal timescales.

The sustained increases in nitrate concentrations are driven not only by higher N inputs but also by structural changes in the landscape, some of which can only be reversed in the long term. Basin-wide conversion of permanent grassland to arable has significantly reduced soil organic matter levels and released mineral N (Whitmore *et al.*, 1992). Soil organic matter takes many decades to accumulate, so reverting arable land to grassland will not reduce nitrate concentrations in the short to

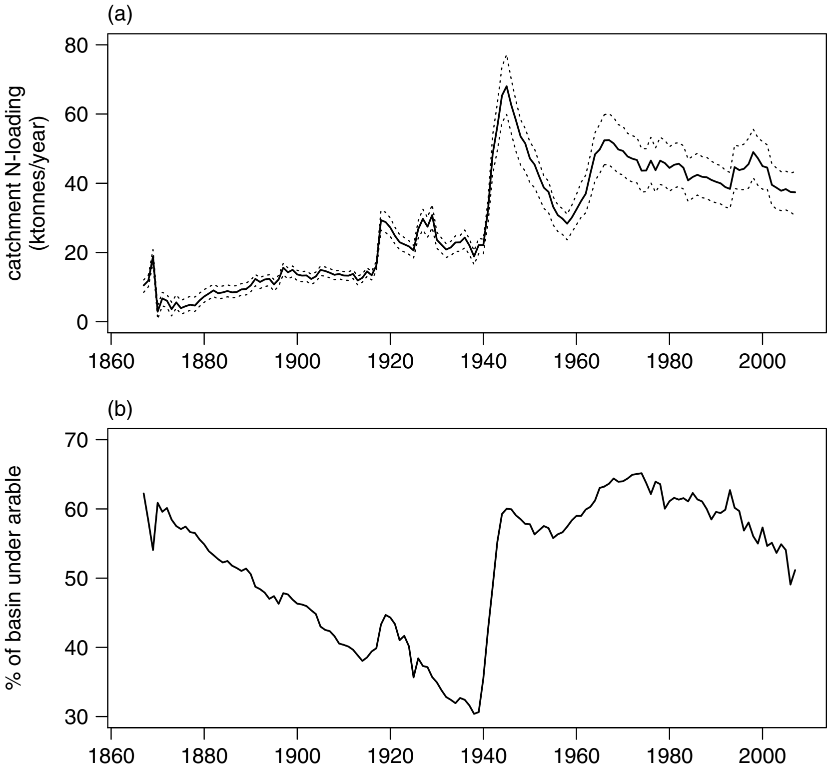

Figure 4. Land use and nitrate loading in the Thames Basin 1868–2008: (a) estimated nitrate loading using the structured model approach (Worrall and Burt, 1999). Mean loading estimate shown as solid line enclosed between dotted lines representing the 5th and 95th estimate percentiles; (b) percentage of the Thames Basin under arable land use 1868–2008: note the abrupt changes during the two World Wars and the gradual increase during agricultural intensification of the 1960s

medium term. Land drainage results in drier soils, enhanced nitrogen turnover and reduced denitrification; moreover, field drains also transfer leached nitrate rapidly to the surface water network, reducing the potential for riparian zone denitrification (Burt and Pinay, 2005). Removal of other landscape barriers (e.g. hedgerows and ponds) has exacerbated this effect. Such fundamental alterations to the fabric of the land mean that the observed high nitrate concentrations will remain high unless very radical changes are made (e.g. 'setting aside' large areas; *cf* Johnson, 1991). Merely reducing nitrogen inputs will be ineffective, as indicated by the lack of a significant downward shift in fluvial nitrate concentrations since 1980.

We draw four conclusions from our analysis of this unique water quality record.

1. **The 140-year-old Thames record indicates that, once a step change has occurred, nitrate concentrations remain intractably high despite large-scale and sustained management intervention.The main driver of change is land use but present nitrate concentrations continue to reflect historical events (i.e. from the 1960s and before) rather than more recent farming practice. These changes are irreversible unless a significant area of arable is converted, in the long term, to grassland or woodland and landscapes structures are restored (to include removing drains from floodplains).**
2. **Present policies for controlling nitrate pollution are fundamentally flawed because they address only a short-term component of the problem (i.e. fertilizer management). We urge caution before implementing policies (usually market-driven) that encourage massive land conversions (Hill *et al.*, 2006; Mulholland *et al.*, 2008) as their impact on fresh and marine waters could persist for many decades.**
3. **Because the Thames record shows no system recovery in the last 40 years, conclusions drawn from short-term monitoring, certainly less than 15 years, could be erroneous unless viewed in an appropriate historical context (Burt *et al.*, 2008, 2010). We recommend that, in any region, a few, very long benchmark monitoring sites must be maintained to provide this context.**
4. **The effects noticed by others in very small streams (Mulholland *et al.*, 2008; Brookshire *et al.*, 2009) are here evident at an intermediate basin scale and indicate progressive downstream reduction in the efficacy of rivers as nitrogen sinks, resulting in increased export to estuaries, coastal waters and oceans. In comparison with the world's largest**

river basins (e.g. the Mississippi, Nile, Amazon: all >1 Mkm^2), the Thames is relatively small (9850 km^2), such that the effects described here may be masked at larger scales. This underlines the need to monitor tributary basins, not just the main river.

The dynamic metastability (Chorley and Kennedy, 1971) of the Thames record shows what can happen to the water quality in response to large-scale land conversion. This warns of the long-term consequences of short-term gain and adds a new dimension to the management imperative of controlling nitrogen loading to streams and rivers, particularly given the prospect of global agricultural intensification to feed a 50% larger world population by the middle of the century.

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