STREAM WATER QUALITY IN THE SLAPTON CATCHMENTS: A META-ANALYSIS OF KEY TRENDS SINCE 1970

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A weekly programme of water quality monitoring has been undertaken by the FSC's Field Centre at Slapton Ley since 1970. Samples have been collected from the main streams draining into the Ley and from the Ley itself. The main purpose of this paper is to make available an online archive but in so doing the opportunity has been taken to update previous publications. Not surprisingly, given the ongoing eutrophic status of the Ley, most attention has been paid to the nutrients nitrate and phosphate; this review broadens the scope to include other water quality records. In relation to eutrophication, there are clear signs of improvement in the influent streams, but concerns remain about water quality in the Ley itself.

INTRODUCTION

Small, low-order, headwater streams play essential roles in providing natural flood control, trapping sediments and contaminants, retaining nutrients, and maintaining biological diversity (Riley *et al.*, 2018). The river continuum concept emphasises that the influence of headwater processes extends into downstream reaches, lakes and estuaries (Vannote *et al.,* 1980). However, the large geographical extent and the high connectivity of these small, headwater streams to their surrounding terrestrial ecosystems makes them particularly vulnerable to growing land-use pressures and environmental change, from agriculture in particular. The extensive length of the low-order stream network exposes these streams to a wide range of inputs, including nutrients, pesticides, heavy metals, sediment and other contaminants (Riley *et al*., 2018). Evidence shows large variability of nutrient fluxes from small tributary basins, but little variability from the entire river basin (Burt and Pinay, 2005). In other words, the signal-to-noise ratio is low in large basins but high in small tributaries (Strayer, *et al*., 2003); this means that subtle changes in land-management practices cannot be detected at the outlet of large basins. It follows that lumped or 'black box' models (which lack spatial detail) cannot be used in large river basins to show where, when and by how much a given policy might affect nutrient fluxes as a result of changes in land management, since they are not sensitive to local conditions. This points towards the need for a spatially explicit approach at the landscape scale.

There was concern in the 1960s that Slapton Ley, a freshwater coastal lagoon and the largest natural body of fresh water in south-west England, was becoming increasingly eutrophic. Eutrophication arises from a disproportionate supply of nutrients. Nutrient enrichment induces excessive growth of plants and algae and can result in oxygen depletion of the water body. Phosphorus is usually identified as the primary limiting nutrient although excessive amounts of nitrate are also influential. The increased influx of nitrogen into the terrestrial biosphere has led to *inter alia*: lowered drinking water quality; loss of habitat; low dissolved oxygen levels; and increased occurrence of algal blooms (Burt and Worrall, 2009). In order to be able to quantify inputs of water, sediment and nutrients into Slapton Ley, a programme of continuous stream discharge monitoring and weekly water quality sampling was initiated in 1969. Water quality data are available for the main streams that flow into the lake from September 1970. The sampling regime included both the two larger (higher-order) rivers flowing into the lake and two first-order streams.

The purpose of this paper is to accompany on-line publication of the water quality data for the Slapton catchments in the hope that researchers will explore the data set beyond what has already been analysed and published (see the reference list at the end of this paper). For that reason, the meta-analyses presented here are partial in their coverage and by no means exhaustive; some long-term trends are explored, an obvious focus given the remarkable length of these time series in the context of small catchment research.

SITE HISTORY AND METHODS

The location of the Slapton Ley catchment and of the water sampling sites is shown in Figure 1. The major rivers and stream draining into Slapton Ley have been gauged from the early 1970s; full details are given in van Vlymen (1979). Of these, the largest is the River Gara with a catchment area of 23 km^2 at the Higher North Mill (HNM) gauging station. Whilst this is larger than the c.10 km^2 threshold which is often identified for "headwater streams" (Jarvie *et al*., 2018), it is nevertheless small by most standards; the other influent streams to Slapton Ley are smaller headwater streams. The Slapton Wood (SW) stream joins the Gara further downstream. Whilst only 1 km^2 in area, this basin is of some significance because of the detailed hydrological research carried out there (Burt *et al*., 1983; Burt and Butcher, 1985; Burt and Arkell, 1987). The River Gara drains though the Higher Ley (0.14 km^2) to reach the Lower Ley; the Higher Ley is now mainly reed swamp with an open channel flowing through it, having been largely open water in 1945. The Lower Ley (0.77 km^2) comprises open water fringed by reed swamp or marsh; its maximum depth is 2.9 m. The Start (10.8 km^2) and Stokeley Barton (1.5 km^2) streams both drain directly into the Lower Ley. The Lower Ley drains through a culvert at Torcross when the water level is high enough; otherwise, drainage is by seepage through the shingle ridge into the sea. In total, the catchment area is 46 km^2 of which 81% is gauged (van Vlymen, 1979). Although a complete record of stream discharge has never been compiled, the stage height associated with water sampling is always noted. The soils of the Slapton Wood catchment are described in Trudgill (1983).

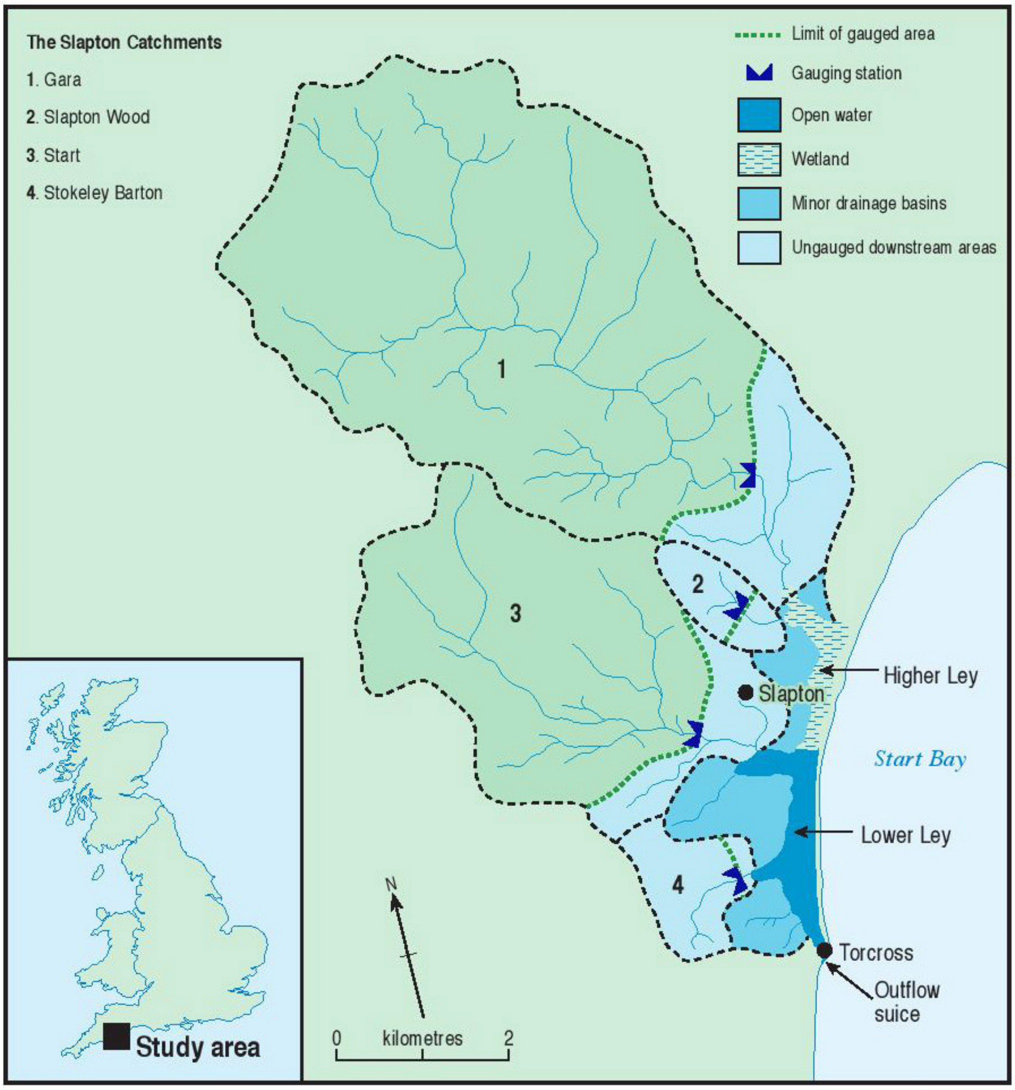

FIGURE 1. Schematic map of the Slapton Ley catchments.

Water samples (collected by hand) are first recorded in the FSC Field Centre ledgers on 7th September 1970 for three of the streams but not the Start, where the first recorded sample is 1st January 1972; earlier data for the Start have been estimated from the Gara results. Note that, although the sampling frequency is weekly, the analysis here is for monthly averages, because this gets over any problems of missing data and generally makes patterns easier to identify and interpret. To our knowledge, no water quality data collected by Slapton Ley Field Centre (SLFC) are available for the Ley itself until 20th December 1978. It is not clear whether samples were collected before that, but there is no mention in Duckworth (1979) who was first to collate nitrate data from the Slapton catchments. Some independent data are available from the Environment Agency (EA) from April 1975, with a more complete coverage by the EA of determinands from 1990. A full suite of meteorological observations has been made daily at the FSC Field Centre in Slapton village since spring 1960 (Burt and Horton, 2001: https://www.slnnr.org.uk/research/weather-data.aspx).

One important aspect is, of course, data quality assurance. Straightforward measurements of water quality have always been made at the Slapton Ley Field Centre (SLFC), such as pH and electrical conductivity. Even with these parameters, problems can arise if calibration procedures are not followed or defective probes not replaced. The water chemistry analyses for nutrients have always been made off site through the good offices of various universities over time: Exeter University, Seale Hayne College (now University of Plymouth), the University of Plymouth itself and, since 2005, Durham University. Potential issues here relate to sample storage and transportation. Of course, analytical techniques have changed over nearly five decades. Originally, analysis would have been by flame photometer, then by atomic absorption spectrophotometry, and more recently also by ion-selective probe. Most recently at Durham, analysis of water chemistry (cations and anions) has been done by ion chromatography (*Dionex*). Changes in analytical techniques over the decades may have led to inhomogeneities in the record. Where a SLFC time series appears not to be homogenous, reference is made to Environment Agency data, less frequently sampled (roughly monthly) but, we assume, analysed to consistently high standards as required by the Water Framework Directive (APEM 2015). The examples below use both SLFC and EA data as appropriate.

The results presented here include the application of a novel nutrient limitation assessment methodology to explore the extent to which nutrients may potentially limit primary production in headwater streams and rivers (Jarvie *et al*., 2018). This involves coupling ternary assessment of N, P and carbon (C) concentrations, with N:P stoichiometry, and threshold P and N concentrations. Readers are referred to Jarvie *et al*. (2018) for a full description of this approach. In relation to this article, the following notes are relevant:

1. The longer-term EA data for the River Gara at Higher North Mill (HNM; 1974 - present) only had nitrate-N (NO_3-N) measurements; longer-term nitrite (NO_2-N) or total oxidized nitrogen (TON = NO_3-N + NO_2-N) were not always available. Therefore, NO_3-N concentrations were used in the ternary diagrams and analysis.
2. For the Ley samples, where NO_3-N was not available, TON values were used. An analysis of samples where both NO_2-N and NO_3-N were measured showed that NO_2-N contributes only a very small (usually negligible) proportion of the TON (median 0.7% of TON; mean 3% of TON).
3. EA data for reactive phosphorus (RP) and NO_3-N concentrations up to 2018 were used for this section of the analysis.
4. Dissolved Inorganic Carbon concentrations were calculated from pH, alkalinity, and water temperature measurements, using the THINCARB model (Jarvie *et al*., 2017)
5. Since the Redfield (1958) C:N:P ratio of 106:16:1 is a molar ratio, the lake and river C:N:P values are reported as molar ratios.

LONG-TERM TRENDS IN WATER QUALITY IN THE SLAPTON CATCHMENTS

Electrical conductivity

Figure 2 shows electrical conductivity (EC; sometimes known as specific conductance) for the River Gara at HNM, the largest influent stream to Slapton Ley; both EA and SLFC data are plotted. EC is a measure of a solution's ability to conduct electricity and reflects the total dissolved solids concentration of the water sample; EC is strongly associated with the major ions such as calcium, sodium, chloride and sulphate. Note that the EA data are spot samples whereas SLFC data are monthly averages, usually of four or five samples. Whilst there are some differences between the two time series, they are broadly similar. Differences in the 1980s might possibly relate to a poorly calibrated probe at the Field Centre or it may real difference because of the greater frequency of observations. Differences after 2007 coincide with the EA's change to a 25 °C calibration rather than 20 °C as still used at the Field Centre. An upward trend in the EA data may therefore be caused by the change in measurement protocol towards the end of the time series. The average EC values are 292 µS and 263 µS for the FSC and EA data respectively, indicating a relatively low solute content, consistent with a low alkalinity status (see below).

EC data for Slapton Ley itself indicate slightly higher values than for the River Gara: SLFC data average 352 µS since 1982; the average for EA data is 303 µS. There is a downward trend for field centre data but not for the EA data (Figure 3).

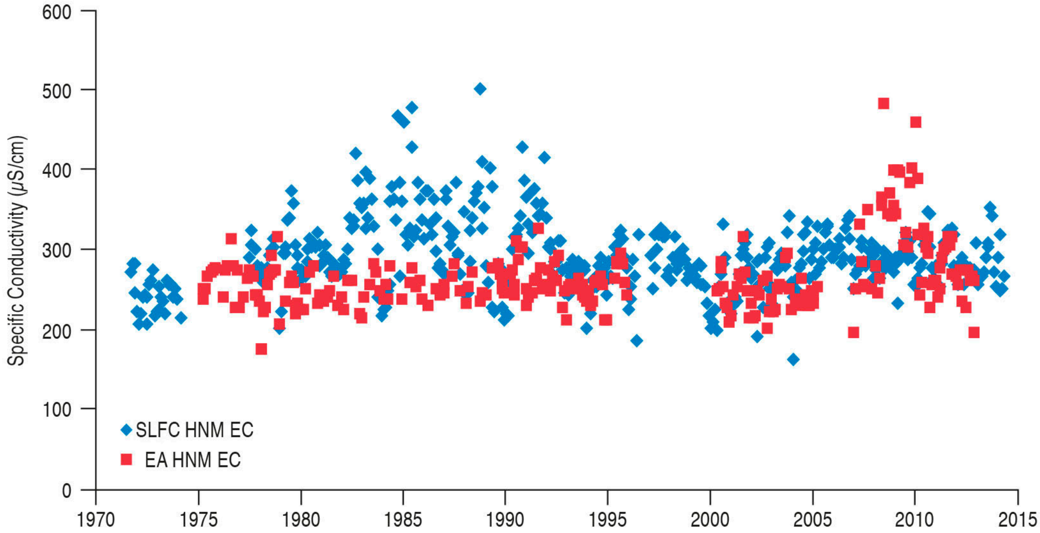

FIGURE 2. Electrical conductivity for the River Gara at Higher North Mill; both Environment Agency (EA) and SLFC data are plotted.

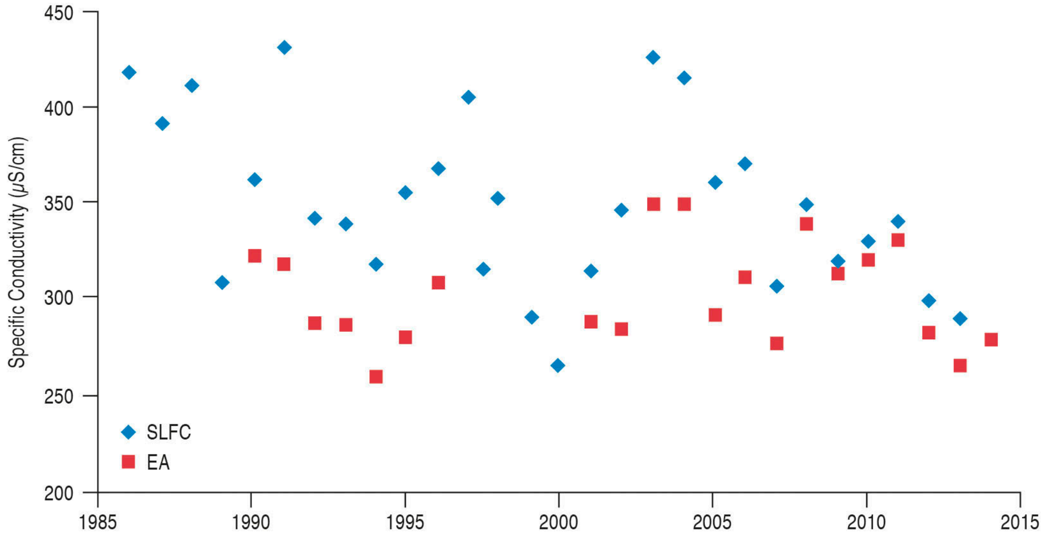

FIGURE 3. Annual averages of electrical conductivity for the Lower Ley; both Environment Agency (EA) and SLFC data are plotted.

pH

We have some doubts about the accuracy of the SLFC pH data which show a downward trend from 2000 not seen in the EA data set. Accordingly, here we just use the EA data for Slapton Ley. Figure 4a shows annual average pH, indicating a gradual rise over four decades. The overage average is 8.2, indicating mildly alkaline conditions. Figure 4b shows monthly averages, with a clear seasonality: lowest, near-neutral values in winter and highest pH in summer. Alkalinity increases in summer because plants and algae remove CO_2 from the lake water for photosynthesis, raising pH as a result, in some cases over pH 10 (Scott *et al*., 2005). Figure 4c shows average summer pH in the lake. In the current management plan for the National Nature Reserve, the target pH for the Lower Ley in summer is an average below 9: this target has only been met once since 1998.

Figure 5 shows pH for the River Gara at Higher North Mill (EA data, n=376). The Gara pH is a generally a little lower than the lake (average 7.9). This could be the result of differences between inputs from the different sub-catchments (Figure 1) or may reflect within-lake processes as described above.

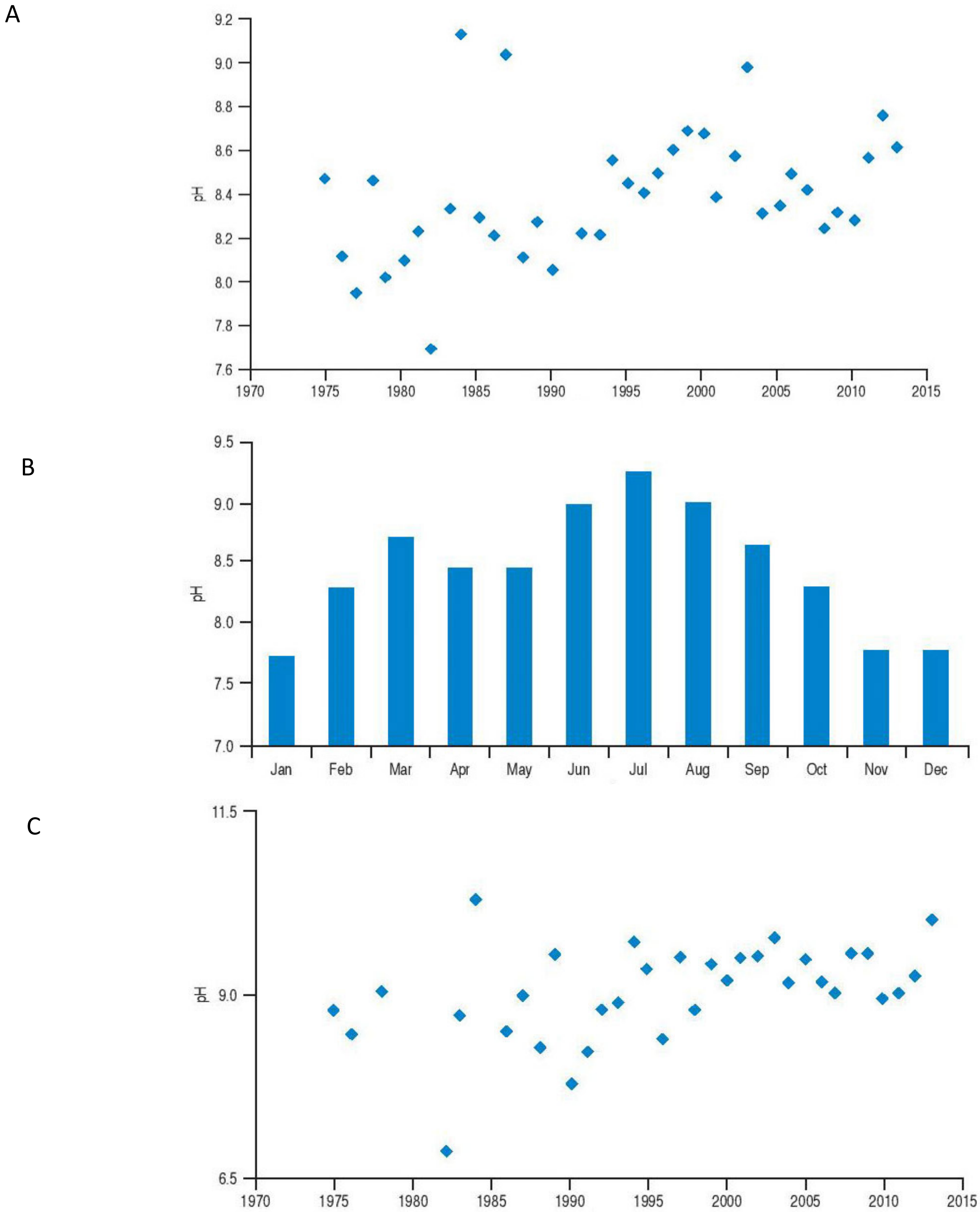

FIGURE 4. Environment Agency (EA) pH data for the Lower Ley: averages (A) annual; (B) monthly; (C) summer.

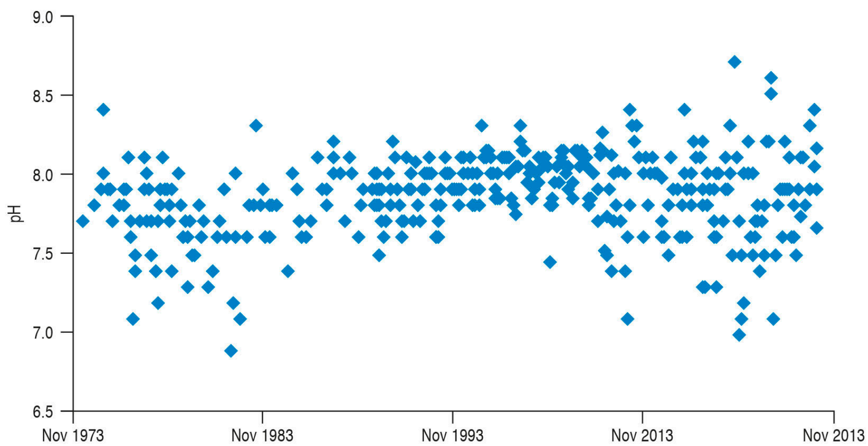

FIGURE 5. Environment Agency (EA) pH data for the River Gara at Higher North Mill.

Alkalinity

No SLFC data are available for alkalinity. The unit of measurement for EA alkalinity data is *alkalinity to pH 4.5 as $CaCO_3$*. Alkalinity averages 67 for the River Gara and 77 for the Lower Ley, in line with the pH results. Figure 6 shows EA alkalinity data for the Lower Ley. The same very gradual upward trend is apparent as in previous graphs; the trend is just statistically significant at p=0.05 but this is largely a result of the large sample number (n = 336).

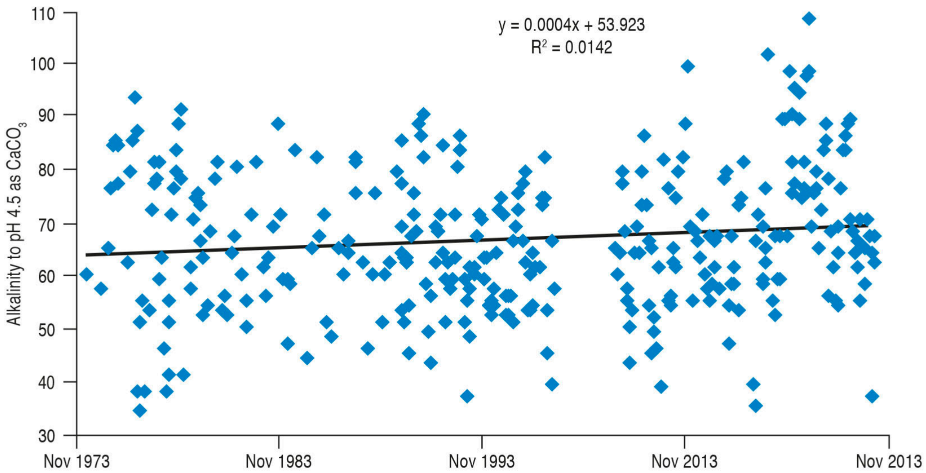

FIGURE 6. Environment Agency (EA) alkalinity data (*alkalinity to pH 4.5 as $CaCO_3$*) for the Lower Ley.

Cations and anions

As an illustration of the correlation between individual ions, Table 1 shows significant correlations for data from the River Gara from the period 2013 to 2017 (n = 192). Samples collected weekly are analysed in 6-week batches; two data sets are missing, in one case water bottles having been broken in transit and in the other the cation results were set aside as unreliable. We have also excluded phosphate results as the levels in 2016 seem an order of magnitude too high. Calcium (average 27.1 mg/l) and magnesium (average 6.6 mg/l) show a very similar pattern of correlation, being highly correlated with each other. They are strongly correlated with other ions except potassium and nitrate. Sodium (average 13.8 mg/l) correlates strongly with other cations but somewhat less strongly with anions including chloride. Potassium (average 1.9 mg/l) has a rather different pattern of correlations, as expected (Stott and Burt, 1997); the negative correlation with nitrate could suggest that potassium (average 2.2 mg/l) increases in concentration during storm events whilst nitrate (as N, average 4.0 mg/l) is diluted, but neither is significantly correlated with stage height (a proxy for stream discharge). Sulphate (as S, average 3.6 mg/l) is more strongly correlated with other ions compared to chloride despite its much lower average concentration. Some of these associations are to be expected: for example, Ca and Mg are likely to be controlled by the same geochemical drivers at this timescale. Other correlations (or lack of them) are less easy to understand and deserve further investigation. Where significant, the negative correlations with stage height show a strong hydroclimatological control of river solute concentrations: dilution at high flow and the highest concentrations at low baseflow. Figure 7 shows how calcium concentrations dilute at high flow. Baseflow concentrations tend to vary, particularly controlled by differences between seasons and years. Here, the highest baseflow concentrations are from spring 2016; it is not clear why concentrations were higher then than in other low-flow periods, perhaps relating to earlier dry periods and the build-up of calcium in the soil for later leaching into the river. The lowest stage plotted came at the start of the record after a prolonged dry spell, but calcium concentrations were not abnormally high despite this.

Table 1: Correlations between selected ions, 2013-2017 (n=192). Normal font shows correlations significant at p=0.05; italic font shows correlations significant at p=0.01; bold font shows correlations significant at p=0.001; n.s. indicates no significant correlation; blank cells have no results.

	Stage (mm)	Cl	NO3-N	S	Na	K	Mg
Chloride (Cl)	**-0.37**						
Nitrate (NO3-N)	n.s	0.15					
Sulphate (S)	**-0.59**	**0.32**	n.s.				
Sodium (Na)	*-0.19*	*0.22*	*0.20*	**0.39**			
Potassium (K)	n.s	n.s.	**-0.57**	n.s.	**-0.51**		
Magnesium (Mg)	**-0.83**	**0.44**	0.18	**0.64**	**0.40**	n.s.	
Calcium (Ca)	**-0.74**	**0.47**	n.s.	**0.64**	**0.38**	n.s.	**0.90**

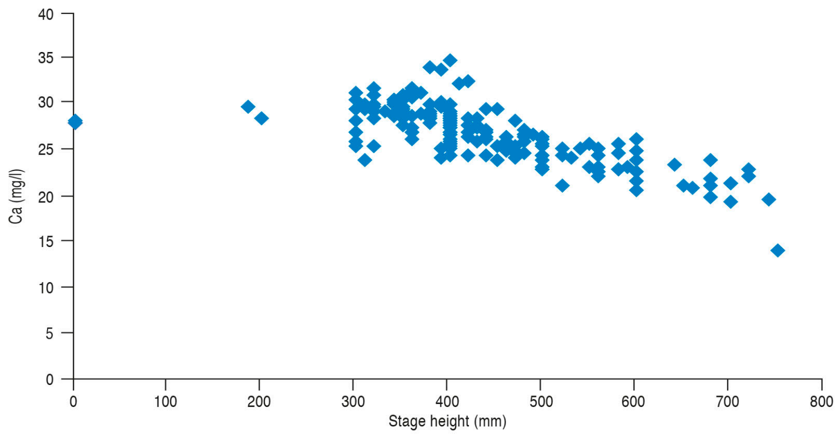

FIGURE 7. Calcium concentrations at HNM in relation to river flow (for which the surrogate *stage height* is used).

Figure 8 shows monthly averages of calcium concentration for the River Gara at Higher North Mill since 1970. Note that data from 2002 to 2007 have been excluded because the values seemed much too high, values between 40 and 90 mg/l much higher than anything else in the record. The values between 1985 and 1989 seem too low, although no lower than for the early 1970s. This record illustrates the difficulty of using long records where different measurement methods have been used over time, and in different laboratories. If the record is reliable, then there seems to have been a gradual increase in calcium concentrations over time. Is this a response to changing climatic conditions or to some change in land management, or both? Figure 9 shows the comparable River Gara record for magnesium. Again values are lower in the latter half of the 1980s. Some very high values have been excluded for the first 6 months of 2002 but after that, unlike calcium, concentrations quickly returned to the usual level for magnesium. The important point about Figure 9 is that, unlike calcium, there is no long-term upward trend. Does this mean a differential response for the two cations or does this cast some doubt on the early calcium record?

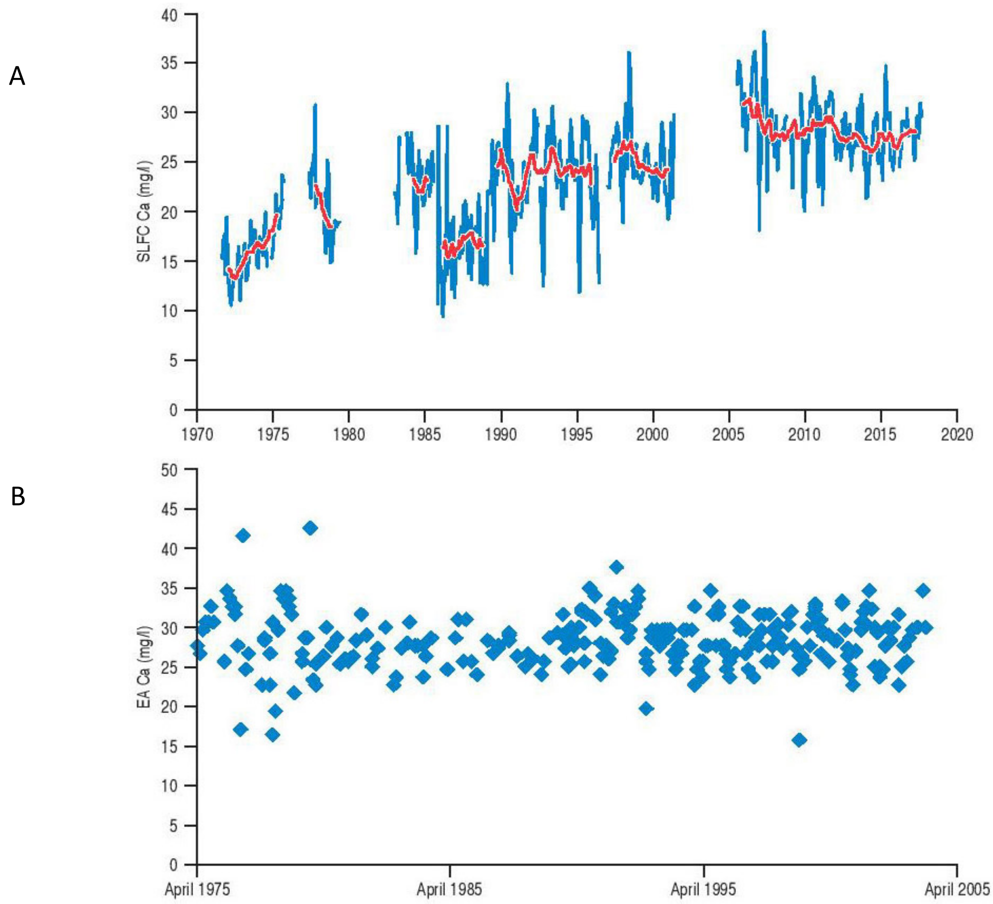

FIGURE 8. Monthly averages of calcium concentration for the River Gara at Higher North Mill since 1970: (A) SLFC data, (B) EA data.

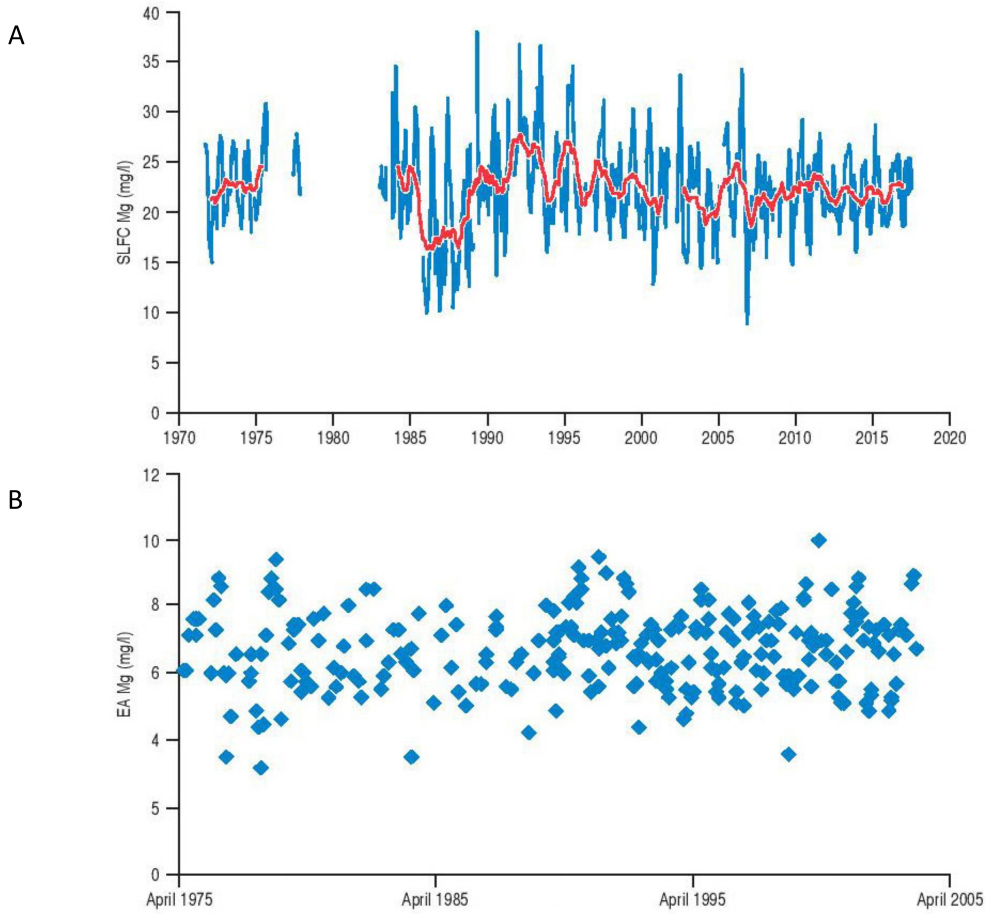

FIGURE 9. Monthly averages of magnesium concentration for the River Gara at Higher North Mill since 1970: (A) SLFC data, (B) EA data.

Nitrate

The nitrate record for the Slapton Ley catchment has been the subject of more research than any other water quality determinand, beginning with the study of stream nitrate loads by Troake *et al*. (1976). Burt *et al*. (1988) reported stream nitrate levels in the Slapton Wood catchment, a small catchment of mixed land use, over a period of 15 years (1970–1985). They noted that a data record of this duration was possibly unique at the time in the United Kingdom for such a small basin (94 ha). At the time the paper was published (1988), there was concern about a trend of rising nitrate concentrations, an issue in most lowland rivers in the UK in the latter part of the twentieth century (cf. Howden *et al*., 2010). Burt and Worrall (2009) revisited the original Slapton Wood time series and subjected it to a more detailed time series analysis than performed in any of the previous studies. They noted that the upward trend had not continued in the last two decades and that nitrate concentration in the catchment seemed to have reached a new equilibrium. Since then, concentrations have begun to gradually decline, a pattern seen in all the influent streams to the Ley. Figure 10A shows the monthly average nitrate concentration (based on four or five weekly samples, SLFC data) for the River Gara at Higher North Mill. There are three main phases: rising concentrations to the late 1980s; then, a period of variability but no long-term trend; finally, falling concentrations from around 2005. It is worth noting that the recent decline has been greater in the Slapton Wood catchment (Figure 10B), starting from a higher concentration. This is probably because Loworthy Farm, the main user of land in the Slapton Wood catchment, is no longer producing arable crops so the intensity of land use has fallen significantly. Whilst there has been no similar dramatic change in land use across the rest of the Gara catchment, there may well have been reductions in inorganic fertiliser application; agriculture is the main supplier of nitrate load to the Slapton streams (Burt *et al*., 1996). Further work is needed to survey farming practice across the catchment in order to update previous surveys (e.g. Johnes and O'Sullivan, 1989). Note that concentrations have generally been higher in the Slapton Wood stream, reflecting the lowland arable land use. The Gara catchment includes land where agriculture is less intense in response to higher altitude, slightly cooler temperatures and higher rainfall; grassland tends to be more common higher up the catchment therefore.

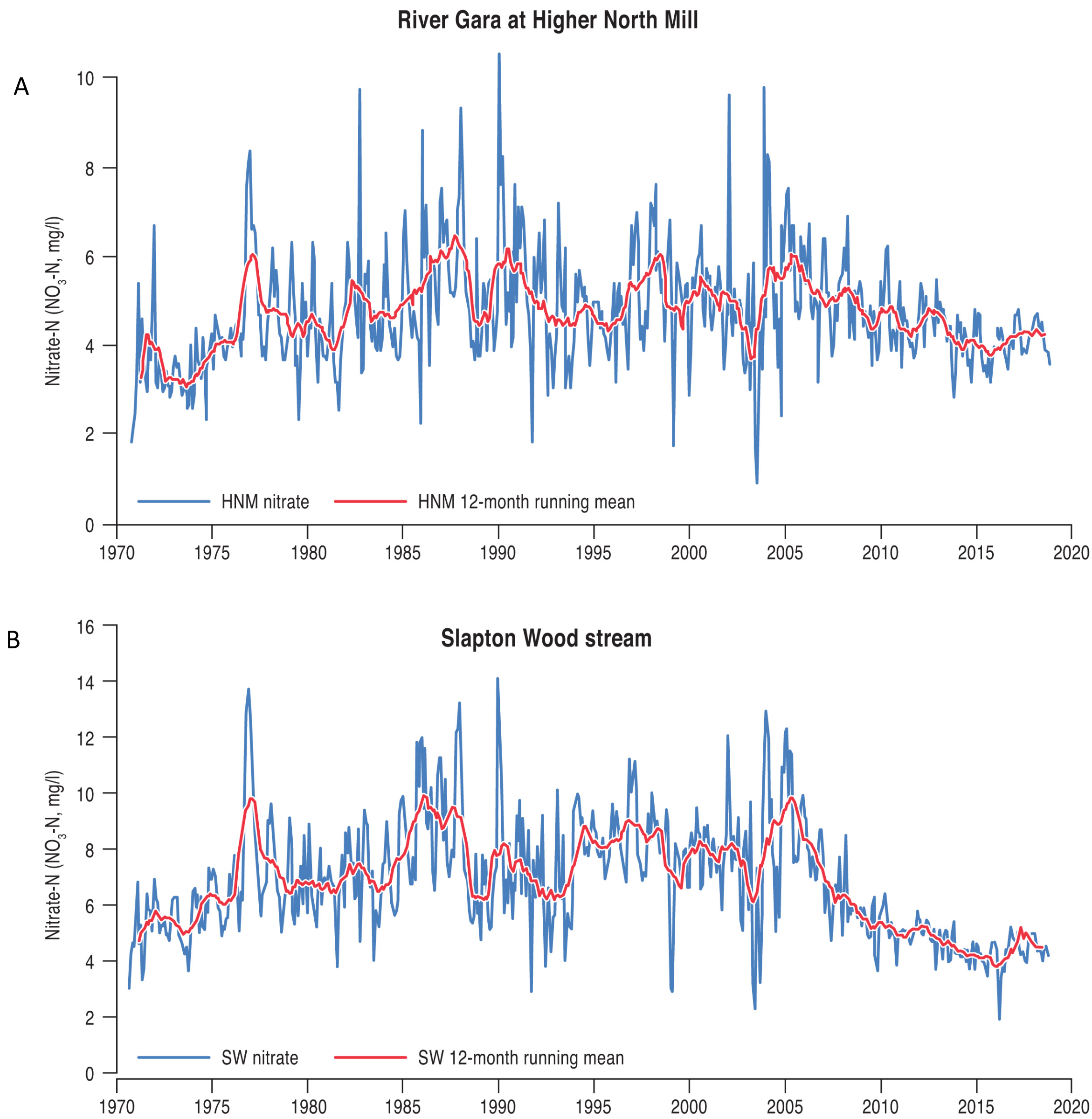

FIGURE 10. (A) Monthly average nitrate concentrations for the River Gara at Higher North Mill (blue line) plus a 12-month running mean (red line); (B) Monthly average nitrate concentrations for the Slapton Wood stream (blue line) plus a 12-month running mean (red line).

Figure 11 shows the monthly nitrate record for Slapton Ley itself. It is not clear why this record only starts in late 1978. Duckworth (1979), who analysed the first eight years of nitrate concentrations in the Slapton streams, does not present any nitrate data for the Ley; nor do Troake *et al*. (1976). Either the lake was not included in the weekly sampling programme until 1978 or, perhaps more likely, earlier records have been mislaid. What is immediately striking about the nitrate record for the Ley is its strongly seasonal nature with concentrations falling below the detection limit in most summers; the very wet summer of 2012 is one of the few exceptions. It is possible that nitrate sometimes becomes the limiting nutrient during summer therefore, but high-frequency measurement of lake water quality would be needed to test this idea. There are several cases from around the world where adding nitrogen may have actually reduced symptoms of eutrophication, either by increasing the N:P ratio to values that allow more desirable species to outcompete cyanobacteria, or by acting as an electron acceptor that inhibits the release of phosphorus release from sediments (Schindler *et al*., 2016).

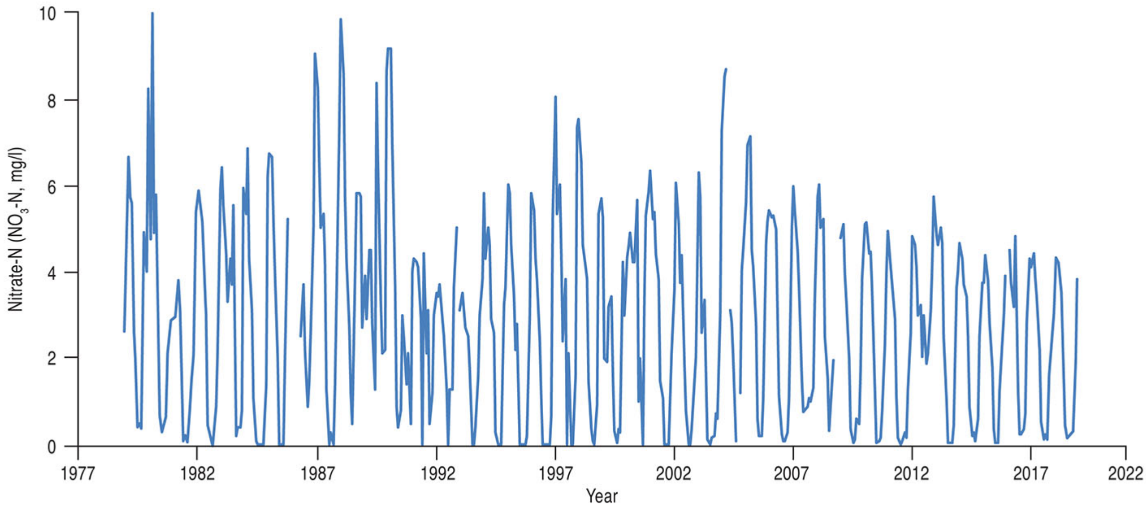

FIGURE 11. Monthly average nitrate concentrations for the Lower Ley.

Phosphorus

Global food production depends on phosphorus (P). Phosphorus is broadly applied as fertilizer, but excess phosphorus contributes to eutrophication of surface water bodies and coastal ecosystems (Powers *et al*., 2016). As human populations increase and land use intensifies, toxic and unsightly nuisance blooms of algae are becoming larger and more frequent in freshwater lakes with blue-green algae (Cyanobacteria) favoured by low ratios of nitrogen to phosphorus. In the past half century, aquatic scientists have devoted much effort to understanding the causes of such blooms and how they can be prevented or reduced (Schindler *et al*., 2016). Phosphorus is a necessary nutrient for plants to live, it is a limiting factor for plant growth in many freshwater ecosystems and a major cause of lake eutrophication. The availability of phosphorus generally promotes excessive plant growth and impairment of water quality. In general, excess phosphorus inputs to water bodies usually come from sewage, industrial discharges or agricultural runoff. There is no significant industrial source of phosphorus in the Slapton catchments, and sewage effluent has been limited in recent years; importantly, a phosphate stripper at the Slapton sewage treatment works (STW) was installed in 1995 and in 2004 a new scheme was installed to transfer the effluent to Torcross for discharge via the existing sea outfall. It may well be that agriculture has become a relatively more important source in recent years therefore.

Within lakes, storage of P in sediments and seasonal recycling can delay recovery from eutrophication (May *et al*, 2012), so that a strong "legacy" effect is observed where, despite reduced inputs to a river basin, water quality can be slow to respond (Sharpley *et al*, 2013; Haygarth *et al*., 2014; Powers *et al*., 2016). Figure 12 shows the EA orthophosphate record for the River Gara (from 1974) and the Lower Ley (from 1992). There has been a welcome decrease in orthophosphate concentrations in the Gara since 1974. This could be for several reasons including better sewage treatment at Blackawton STW and improved septic tank systems across the catchment. In relation to agriculture, as important a P source as humans in the Slapton catchments (Burt *et al*., 1996), this could relate to reduced inorganic fertiliser inputs, more sensitive farming to limit soil erosion and restrict sediment-laden runoff, especially in riparian areas, and fencing to prevent livestock getting into the river. The Lower Ley too has shown clear reductions in orthophosphate (PO_4-P) concentrations. Improvements to sewage treatment at Slapton STW may be critical here. Using the River Phosphorus Calculator (UKTAG, 2014), Water Framework Directive (WFD, Directive 2000/60/EC) class boundary values have been calculated for the River Gara. This identified a concentration of 32 µg/l (0.032 mg/l) PO_4-P as the boundary between "high" and "good" water quality for the Gara. Before 1992, only 4% of samples were of "high" quality with 60% no better than "poor". In contrast, since 2005, 48% of samples have been of "high" quality with only 3% below "good".

The UKTAG (2016) Lake Phosphorus Calculator uses total phosphorus (TP) concentration rather than just orthophosphate concentration; TP comprises both dissolved and particulate P and both organic and inorganic P species. Recently, with regard to achieving "good ecological status" within the Water Framework Directive, the Environment Agency and Natural England used the Calculator to set a TP target for the Lower Ley of 39 µg/l (Jon Grimes, Natural England, pers. comm., 26 January 2018). This is a much more exacting target for the lake compared to the influent streams like the Gara, given that TP includes all P species not just dissolved inorganic orthophosphate. Figure 13 shows the EA's TP record for the Lower Ley, data collected in two tranches between 1994 and 2014. Since summer 2010, 42% samples can be classified as at least "moderate" status with 58% "poor" or worse. The situation does seem to be improving but more data are needed to confirm this. In the period 1994-2010, only one third of samples met this target. The EA data for the period 2010-14, sampled at Torcross, show that concentrations are much higher in summer and early autumn – this is generally when samples fail to meet the WFD target - with only the very wet summer of 2012 the exception.

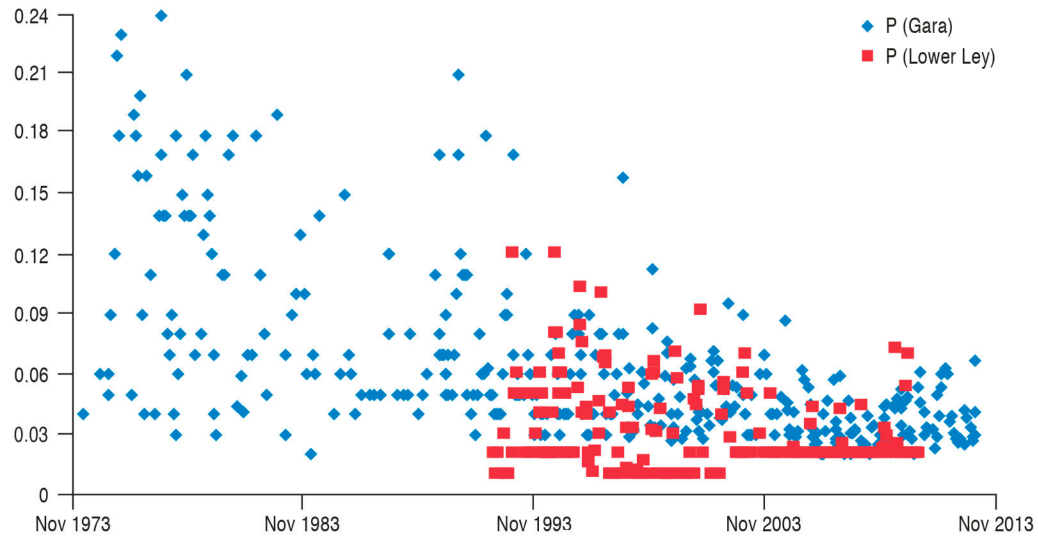

FIGURE 12. Environment Agency (EA) orthophosphate (PO_4) record for the River Gara (from 1974) and the Lower Ley (from 1992).

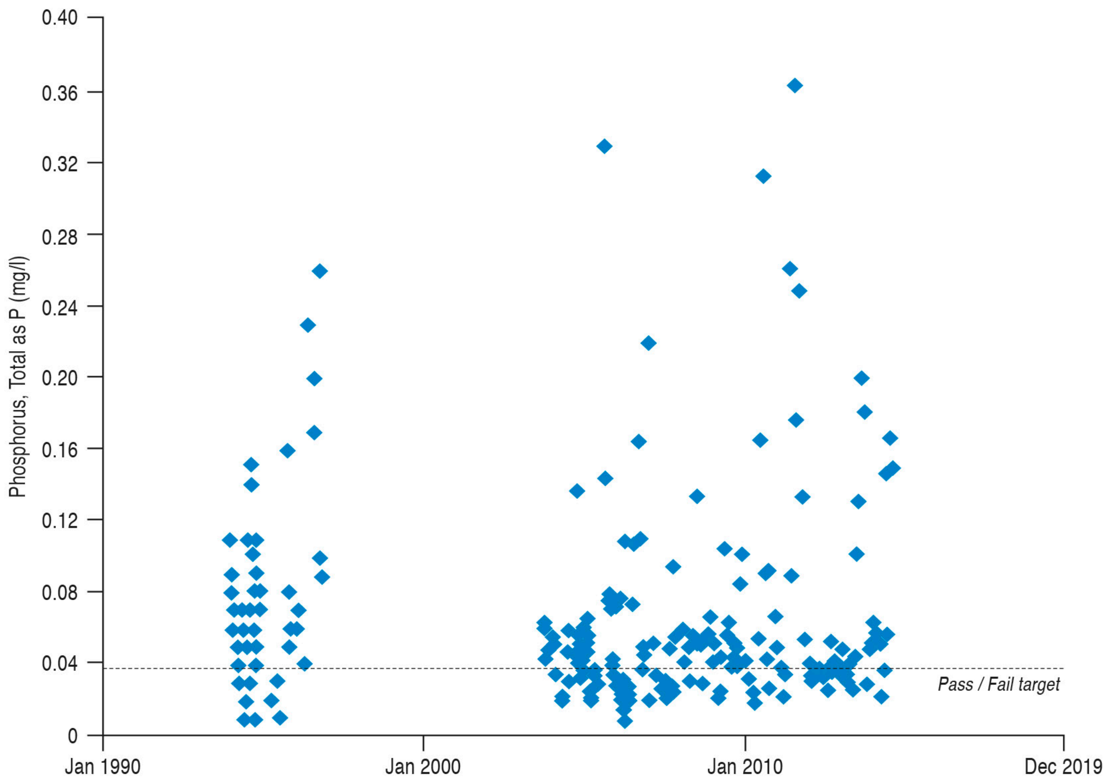

FIGURE 13. The Environment Agency's total phosphorus (TP) record for the Lower Ley.

Coupled ternary assessment of N, P and carbon (C) concentrations

Jarvie *et al*. (2018) applied a novel nutrient limitation assessment methodology to explore the extent to which nutrients may potentially limit primary production in headwater streams and rivers, by coupling ternary assessment of N, P and carbon (C) concentrations, with N:P stoichiometry, and threshold P and N concentrations. In applying this analysis to the Slapton stream and lake water-quality data, ternary diagrams were used to visualise relationships between the major inorganic and readily-bioavailable P, N and C fractions (Smith *et al*., 2017): reactive phosphorus (RP), nitrate (NO_3-N) and dissolved inorganic carbon (DIC). Concentrations were converted to molar units and then transformed (as N_R, P_R and C_R) so that the centre point of the ternary diagram corresponds with the Redfield ratio (1P:16N:106C - Redfield, 1958), which is widely used as a reference 'optimum' P:N:C ratio for primary production. Figure 14 plots the EA data for the River Gara (1974-1999; 2000-2012) at Higher North Mill and for the Lower Ley (1991-2018). The colour of the dots shows the RP concentration (in mg P/l).

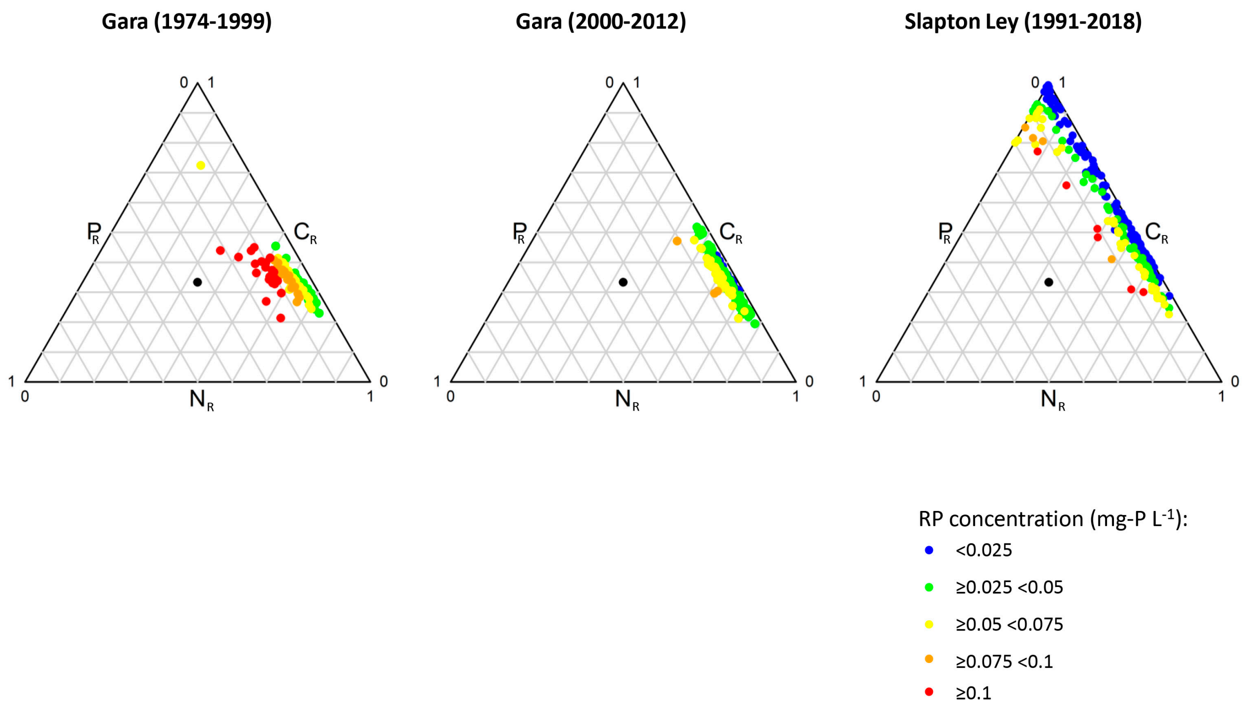

FIGURE 14. Ternary plots showing the relationships between P, N and C in the River Gara and in the Lower Ley. Samples are colour-coded according to their reactive phosphorus concentration. The black circle at the centre of the ternary diagram denotes the Redfield ratio (106C:16N:1P).

All data for the River Gara and Slapton Ley (with the exception of just one pre-2000 Gara sample) plot within the zone of P depletion relative to C and/or N (P_R<0.2). Only one River Gara sample was N and P co-depleted; whereas 26% of Slapton Ley lake samples were N and P co-depleted (at the apex of the triangle, i.e. both N_R and P_R<0.2). For the Gara, it is clear that the latter period had relatively lower P concentrations. For the River Gara prior to 2000, the median concentrations of NO_3-N and RP were 5.2 and 0.06 mg L^{-1} respectively, with a median molar N:P ratio of 180, well above the Redfield 16:1 ratio (Redfield, 1958). From 2000 onwards, the median NO_3-N and RP were 5.25 and 0.04 mg L^{-1} respectively, showing the improvement in river P concentrations, and a consequent increase in the median molar N:P ratio to 330. Before 2000, 34% of Gara samples had RP concentrations indicative of potential P limitation (below an upper limitation threshold of 0.05 mg-P L^{-1}); from 2000 onwards, 75% of Gara samples were indicative of P limitation. The potential for P limitation in the River Gara therefore doubled after 1999.

For lake samples, the median concentrations of NO_3-N and RP were 3.29 and 0.02 mg L^{-1} respectively, with a median molar N:P ratio of 271. 79% of lake observations were indicative of P limitation (<0.05 mg-P L^{-1}); 9% indicative of potential N limitation (<0.4 mg L^{-1}); and 6% indicative of N and P co-limitation. However, corresponding Total N and P measurements would also be needed to confirm limitation effects and overall nutrient supply. This is of particular relevance in standing waters, where low dissolved inorganic nutrient concentrations can reflect high uptake and turnover rates and may underestimate the nutrient supply to the biota. Given that Slapton Ley is shallow, the lake water chemistry generally reflects that of the influent streams, except in summer and early autumn, when inflows are low compared to lake volume. Under these conditions, biological uptake can result in N concentrations falling to potentially limiting levels. Further work is needed to explore the role of in-lake biogeochemical processes, including assimilation, denitrification, the potential for P release at the sediment-water interface, and the possibility that N becomes the limiting nutrient under such conditions. Like the river data, lake P concentrations show a general improvement in P concentrations with 19% observations exceeding 0.05 mg-P L^{-1} before 2000 but only 9% more recently (Gara at SL Site 2 Data).

Despite significant improvements therefore, water quality in the Lower Ley is still very far from "good ecological status" under the EU's WFD. As noted above, P continues to enter the Lower Ley from the influent streams; in addition, P continues to enter the lake water from sediment deposited on the lake bed. If, for example, Loch Leven in Central Scotland is anything to go by, we can expect this "legacy" P to remain important for many years (May *et al*., 2012).

DISCUSSION AND CONCLUSIONS

Given Slapton Ley's ecological importance and its designation as a National Nature Reserve, it is good that there is a strong evidence base concerning water quality in the lake. This comprises the very wide range of measurements undertaken by the Environment Agency (at an approximately monthly frequency) and the weekly samples collected by SLFC since 1970 (APEM 2015). The long, unbroken record is rare for a series of small catchments in the UK. The evidence is clear: water quality in the Lower Ley remains poor, especially in summer, and the appearance of toxic algal blooms shows no signs of abating. Summer pH levels average 9 or above (Figure 4c), a sure sign that algae are removing carbon dioxide from the lake water for photosynthesis. We lack detailed observations from the sediment-water interface, but the strong implication is that phosphorus stored in surface sediments is released by a mixture of desorption and dissolution. P seems to be the main driver of eutrophication, but this may be augmented by very low levels of nitrate in the lake water in summer, encouraging blue-green algae to flourish. It is also clear that we lack data for total phosphorus concentrations in the Lower Ley and it is to be hoped that the Environment Agency can be persuaded to increase the frequency of their measurements, given the NNR's importance.

There is good reason to reduce nitrate concentrations in fresh water, particularly in relation to human health (although this is not directly relevant in the Slapton catchments since drinking water supplies come from outside the catchment). Note that the EU's Nitrate Directive (91/676) targets eutrophication as well as human health, indicating that nitrate is also regarded as a significant pollutant in this regard. Recent evidence of falling nitrate concentrations in Slapton Ley catchment matches observations elsewhere and shows that non-point agricultural sources have less impact than formerly. There may be a small legacy effect in relation to shallow groundwater sources of nitrate (Chappell and Franks, 1996), which can take many years to respond to changes in agricultural practice, but groundwater is a very minor component of the hydrology of the Slapton catchments and so this effect is much less important than in major aquifers like the Chalk (see Howden *et al*., 2010, 2011a, 2011b). Schindler *et al* (2016) note that, in contrast to the lack of evidence for any effect of reducing nitrogen inputs, there are several cases where adding nitrogen has actually reduced symptoms of eutrophication.

Schindler *et al* (2016) review the evidence that P management has been successful in controlling eutrophication. Evidence that reducing inputs of phosphorus is effective in reducing eutrophication comes from four methods, all long-term studies at ecosystem scales: long-term case histories (inadvertent experiments, in effect) and deliberate multi-year whole lake experiments where inputs of phosphorus have been reduced; experiments where chemical treatments are used to remove phosphorus from the water column; and, chemical additions to inhibit return of phosphorus from the sediments to the water column. Careful thought would be needed before any such manipulations could be attempted in Slapton Ley, balancing disturbance against potential gains in terms of significantly improved water quality and any higher-order ecological benefits this might bring. Meanwhile, further evidence is needed of the relevant in-lake processes driving eutrophication, using modern, high-frequency measurement techniques.

Beyond eutrophication, long data series of the type presented here are a rich source for generating new ideas or testing existing hypotheses. This paper has only explored the tip of the iceberg and no doubt many important discoveries are yet to emerge from the Slapton catchment data set. For example, what has driven the gradual increase in base cation concentrations, which seems to be reflected in the electrical conductivity and pH records too? Is there a climatic control or is it connected to change in the way catchment soils are farmed? To encourage new lines of enquiry as well as returning to old ideas in the light of longer records, Slapton Ley Field Centre is pleased to make available both the raw data from its weekly sampling programme and a selection of monthly summary data. Please quote this paper in any publications that result from using these data sets.
https://www.slnnr.org.uk/research/water-quality.aspx

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