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Orthophosphate-P in the nutrient impacted River Taw and its catchment (SW England) between 1990 and 2013†

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Excess dissolved phosphorus (as orthophosphate-P) contributes to reduced river water quality within Europe and elsewhere. This study reports results from analysis of a 23 year (1990–2013) water quality dataset for orthophosphate-P in the rural Taw catchment (SW England). Orthophosphate-P and river flow relationships and temporal variations in orthophosphate-P concentrations indicate the significant contribution of sewage (across the catchment) and industrial effluent (upper R. Taw) to orthophosphate-P concentrations (up to 96%), particularly during the low flow summer months when maximum algal growth occurs. In contrast, concentrations of orthophosphate-P from diffuse sources within the catchment were more important (>80%) at highest river flows. The results from a 3 end-member mixing model incorporating effluent, groundwater and diffuse orthophosphate-P source terms suggested that sewage and/or industrial effluent contributes ≥50% of the orthophosphate-P load for 27–48% of the time across the catchment. The Water Framework Directive (WFD) Phase 2 standards for reactive phosphorus, introduced in 2015, showed the R. Taw to be generally classified as Poor to Moderate Ecological Status, with a Good Status occurring more frequently in the tributary rivers. Failure to achieve Good Ecological Status occurred even though, since the early-2000s, riverine orthophosphate-P concentrations have decreased (although the mechanism(s) responsible for this could not be identified). For the first time it has been demonstrated that sewage and industrial effluent sources of alkalinity to the river can give erroneous boundary concentrations of orthophosphate-P for WFD Ecological Status classification, the extent of which is dependent on the proportion of effluent alkalinity present. This is likely to be a European – wide issue which should be examined in more detail.

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Environmental impact

Excess orthophosphate-P has a detrimental impact on river water quality worldwide. We coupled statutory monitoring data with data mining to quantify point and diffuse sources of orthophosphate-P to rivers within a typical orthophosphate-P impacted rural catchment. This insight highlighted the importance of monitoring the bioavailable P fraction with sufficient temporal and spatial resolution to determine the seasonality of different inputs and the need for targeted, high frequency monitoring of key orthophosphate-P inputs, particularly during low summer flows. It also enhanced our understanding of phosphorus impacts on water quality which allows more effective management of catchments and downstream estuarine and coastal waters. It also demonstrated the impact of effluent alkalinity on river phosphorus standard setting within the Water Framework Directive.

1. Introduction

The deleterious impacts of increased anthropogenic loads of phosphorus, principally as orthophosphate-P, on river water quality within Europe and elsewhere have been recognised for several decades.[3] Within the EU, the Urban Waste Water Treatment Directive (UWWTD, 91/271/EEC) has been the main legislative driver in reducing phosphorus inputs from urban centres to surface waters, largely *via* improved waste water collection and reductions in phosphorus concentrations in sewage treatment work (STW) effluents.[4] Across the EU, decreases in riverine orthophosphate-P concentrations of 2.1% per year on average in the two decades to 2012 have been ascribed to the mitigation measures implemented under the UWWTD.[5,6] The mean orthophosphate-P concentration in *ca.* 1000 EU rivers in 2012 was 0.06 mg P L^{-1}.[5] In the UK, decreasing concentrations since the late 1990s – mid 2000s have been reported for the R. Thames[7,8] and its tributaries,[8] and the Dorset R. Frome.[9,10] In the R. Tamar (south-west England) decreasing concentrations with time were also evident, although reduced sampling frequency in the later stages of the time series reduced confidence in this conclusion.[11]

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The EU Water Framework Directive (WFD; 2000/60/EC) was promulgated with the significant objective to protect, enhance and restore all bodies of surface water with the aim of achieving Good Ecological Status (GES) of surface and ground waters by 2015. Despite the apparent success in reducing riverine orthophosphate-P concentrations there are still many rivers across the EU that are failing to achieve GES for this nutrient, including many in the UK.[4] Surface waters receiving effluents from major UK urban centres have been most impacted, and it is here that most effort has been applied to reduce nutrient inputs from STWs (*e.g.*[7]). In rural catchments with relatively low human populations, however, it has become increasingly apparent that sewage effluents also make an important contribution to riverine orthophosphate-P concentrations, particularly during the lower flow, spring and summer months when in-river algal growth can flourish.[8,9,12,13] While tertiary nutrient stripping is being installed in larger STWs, most STWs in rural catchments are too small for this to be required. Furthermore, septic tanks remain integral to waste disposal for many dwellings in rural areas, and their not insignificant contribution to nutrient loading in surface waters is now recognised.[14]

The river phosphorus (termed reactive phosphorus) concentrations which define the Ecological Status boundaries prescribed in the WFD Phase 2 standards introduced in 2015 are estimates of natural phosphorus concentrations, taking into account the alkalinity (measured as $CaCO_3$) of the river water and the altitude, above sea level, that would be expected in the absence of anthropogenic pressures.[15,16] The hypothesis is that the alkalinity concentration observed is a reflection of natural rock weathering and hydrological processes. In pristine areas, unperturbed by anthropogenic impacts, this is likely to be correct. However, in rivers receiving sewage and industrial effluents, this hypothesis is incorrect, as these effluents can contain substantial quantities of alkalinity (*e.g.*[17,18]). In these rivers, inclusion of sewage alkalinity will serve to increase the concentration of phosphorus defining each Ecological Status boundary, effectively providing a more 'relaxed' standard. The extent of this effect will depend on the relative loads of alkalinity from sub-soil sources and sewage and industrial effluent in a sample; for the same effluent alkalinity load the effect will be less for rivers fed from a chalk aquifer than for rivers fed by low alkalinity groundwater or rivers of low base flow index (BFI). The effect may also be most pronounced in rivers which are dominated by effluent flows during the low river flow periods that typify the summer algal growing season.

The Taw catchment in south west England is a predominantly rural environment with a low population and little industry. Nevertheless, thirteen water bodies across the catchment were failing GES for phosphorus under the WFD Phase 1 cycle.[19] An important aim of the Taw River Improvement Project, a recently completed 2.5 years £1.86 M programme designed to improve ecological status of rivers across the catchment (L. Couldrick, pers. comm.) was to undertake an assessment of river water quality data for phosphorus in the catchment. This study is a contribution to that aim. The specific objectives for the current study were to: (i) quantify temporal trends in orthophosphate-P concentrations between 1990 and 2013, and to apportion orthophosphate-P sources, and (ii) calculate Ecological Status in relation to orthophosphate-P using the WFD Phase 2 standards, and then examine if the effluent component of alkalinity compromises the standards for orthophosphate-P in this catchment, and by implication in catchments across the EU. The second objective provides the first analysis of its kind.

2. Methods

2.1 Study area

The Taw system is part of the North Devon catchment of the UK South West River Basin District[20] and covers an area of 1211 km^2. The R. Taw rises at Taw Head on Dartmoor (altitude 550 m AOD) and flows northward to join the estuary at the tidal limit at Newbridge. The major tributaries are the Mole, the Lapford Yeo and the Little Dart River (Fig. 1). The R. Taw (68%) and the R. Mole (29%) drain 97% of the catchment (Table 1). The mean, maximum and Q_{95} flows reflect the relative size of the drainage basins, with these values highest at Umberleigh, located closest to the tidal limit (Table 1). The river responds quickly to rainfall, with rapid rises in river levels.[21] The river base flow indices are mid-range (0.43–0.47; Table 1), and alluvial deposits in the main river valley may contribute to river flows during dry periods.[21] Catchment geology is dominated by the Carboniferous Bude and Crackington formations, while >95% of the catchment is covered by clay and clay loam soils.[22] About 75% of the catchment area is used for agriculture (59% grassland, 14% arable), 12% woodland and forest and 9% rough grassland.[23] An estimated 77% of the grassland is used for beef cattle and sheep, whilst the remainder is used for dairy cattle.[22] The main areas of population are Barnstaple (population 47 858 in 2009), Braunton (11 491), South Molton (13 576) and Witheridge (2262), as shown in Fig. 1.

2.2 Data resource and general approach

Daily mean river flows (DMFs; calculated from 15 min interval instantaneous flow data over 24 h) were obtained from the Environment Agency (EA) gauging stations (GS) at Umberleigh and Taw Bridge on the R. Taw and Woodleigh on the R. Mole (Table 1 and Fig. 1) from 1990 onwards. Chemical determinand data from 1990, collected for statutory monitoring purposes, were also obtained from the EA WIMS for the sampling sites shown in Fig. 1 and detailed in ESI 1.† Site selection was based on EA evidence, since 2010, of failure of river waters to meet WFD Phase 1 GES for orthophosphate-P because of effluent and diffuse pollution.[19] Sample record end dates occurred between 2006 and 2013, depending on site (ESI 1†). The chemical determinands considered herein are orthophosphate-P and total alkalinity. Orthophosphate-P was determined in the sample supernatant following settlement of suspended particles originally present in the collected water sample. As the supernatant may contain colloids and fine particles, as well as non-orthophosphate 'dissolved' P, the resulting measured P concentrations may represent orthophosphate-P plus P associated with these other components that is measurable by the

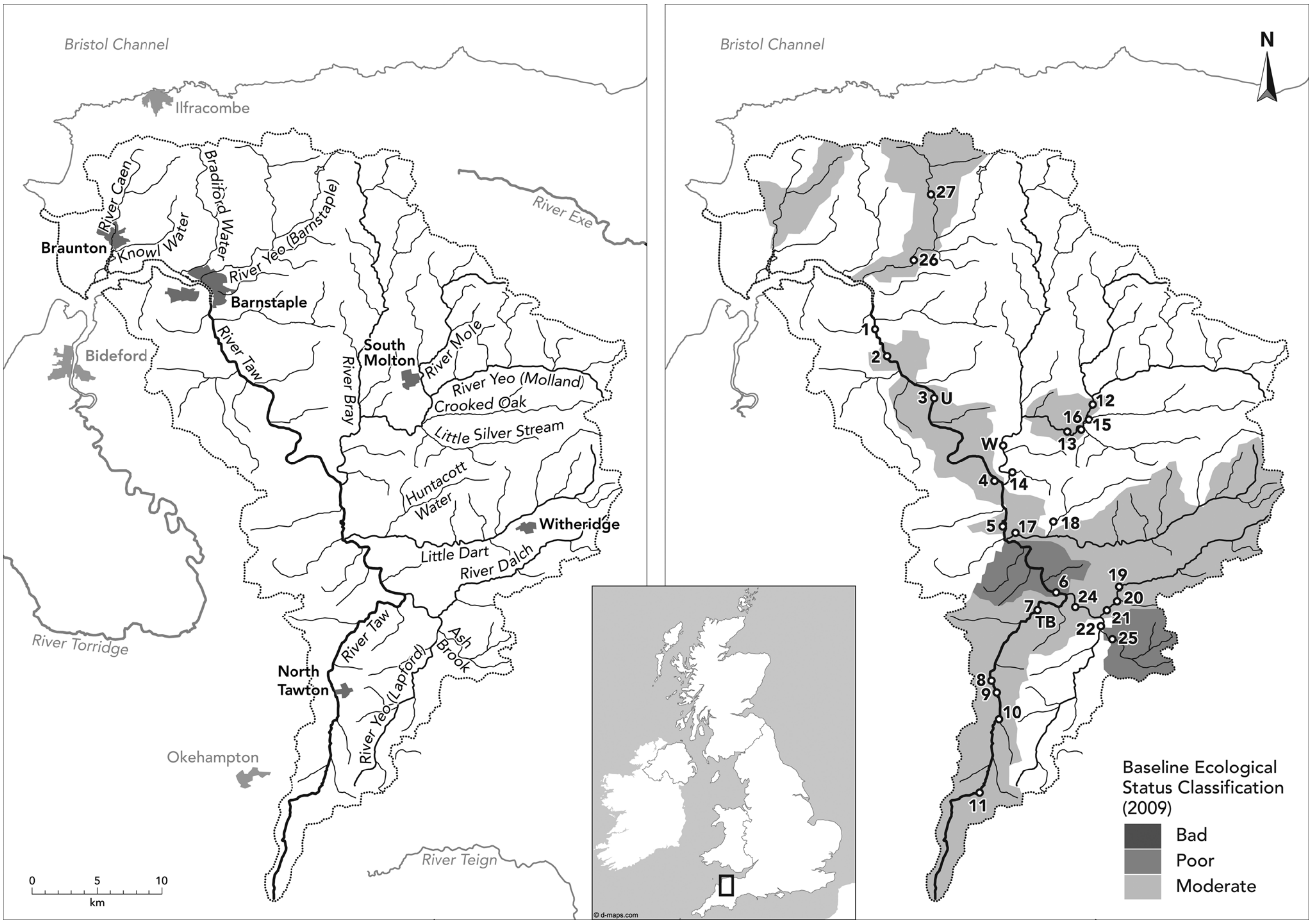


Fig. 1 Left panel: place and river names; right panel: sampling sites (number) and gauging stations (U = Umberleigh, TB = Taw Bridge, W = Woodleigh). The baseline Ecological Status classification of 2009 (ref. 20) is also shown in the right panel.

analytical technique used. As a result, the orthophosphate-P as it is coded in the EA database, may be variously referred to as soluble reactive phosphorus (SRP) or reactive phosphorus (RP). In this paper the term orthophosphate-P is used by default, although the other terms are used when appropriate.

For sites sampled between 1990 and 2013, water samples were collected from a maximum of 4.3% of the 8766 gauged flow days. In general, 4% of the chemical samples were collected within 7 days of each other, 15% within 14 days and 57% within 30 days. Relatively high frequency sampling (25–35 samples per

Table 1 River flow gauging stations included in this study[a]

Gauging station	NRFA station #	% of total catchment drained	Comments	Baseflow index	Daily flow data ($m^3\ s^{-1}$) Mean	Min	Max	Q_{95}
Umberleigh (Taw)	50001	68	Significant modification to flows owing to public water supply abstraction. Augmentation from the Exe catchment at low flows stopped end 2002	0.43	18.0	0.20	364	1.23
Taw Bridge (Taw)	50007	6	Water abstractions at Taw Marsh ceased ~1999. Cheese factory at North Taw bridge abstracts from borehole but also compensates into river at low flow	0.47	1.80	0.02	51.1	0.17
Woodleigh (Mole)	50006	29	Low flows moderately affected by public water supply abstraction and augmentation from Exe-Taw transfers	0.47	8.79	0.20	143	0.87

[a] Data from the National River Flow Archive (NRFA; http://www.ceh.ac.uk/data/nrfa/).

year) was undertaken between 1991 and 1996 at site 2; otherwise the frequency at this site and elsewhere was 10–13 samples per year. Effluent data for STWs in the catchment were provided by the EA; the orthophosphate-P concentration was 5.3 mg P L^{-1} (in the centre of the range of 1–10 mg P L^{-1} for UK sewage effluent[24]) while dry weather flows for each STW were given as an annual mean. The EA also provided effluent orthophosphate-P concentration and flow data for the Taw Valley Creamery, located in the upper catchment between sites 9 and 10 (see Fig. 1), for 2006–2014. There are also many septic tanks throughout the area, which can act as either point or diffuse inputs for nutrients,[14] but there were no data on either flows or nutrient concentrations available for these potential sources.

In Section 3 the data are generally reported for the R. Taw and its tributaries separately. However, at three locations (two on the R. Taw and one on the R. Mole), river flow and chemical concentration data were integrated at each of these locations individually to provide additional insights into orthophosphate-P behaviour; subsequently, the results from these three locations are discussed as a group. For the first location, the flow data from site 3 were combined with the chemical data from site 2, and for the second location chemical data for site 14 were combined with flow data for the Woodleigh GS on the R. Mole. Site 3 is *ca.* 4.5 km upstream of site 2, the most frequently sampled site on the R. Taw, while the Woodleigh GS is *ca.* 4 km upstream of site 14. For the third location, the Taw Bridge GS is co-incident with the chemical sampling at site 7 (Fig. 1). These locations are therefore referred to as site 2, site 14 and site 7. In addition to orthophosphate-P there is also a more extended treatment of the alkalinity data because of the key role of this parameter in the definition of river water quality standards for phosphorus within the WFD.

2.3 Temporal trend statistics and load estimation algorithms

Exploratory data analysis indicated that there appeared to be decreasing trends in orthophosphate-P concentrations in the time series at sites 2, 7 and 14, particularly from *ca.* 2003 onwards. To quantify the potential significance of these patterns at each individual site, temporal trend analyses using the Spearman's Rho, Mann–Kendall and Seasonal Kendall tests were undertaken. These tests are non-parametric, rank-based statistics designed to reveal gradual monotonic trends in time-series data[25,26,28] and are appropriate for relatively coarsely-resolved data.[27] The theoretical basis of the trend statistics are described in Helsel and Hirsch[25] and Hipel and McLeod.[28] The Seasonal Kendall test performs the Mann–Kendall test for individual seasons of the year, where season is defined by the user.[26] The Mann–Kendall and Seasonal Kendall tests require the data to show constant variance through time and to not show autocorrelation.[26,28] Log_{10} transformation of the orthophosphate-P variable satisfied the first assumption, while autocorrelation function analysis showed that the orthophosphate-P data were largely within the limits of acceptable autocorrelation. Autocorrelation is less likely to be observed in monthly resolved data of up to 10 years duration, as is the case here.[26,27] Trend analyses were undertaken on both non flow-adjusted orthophosphate-P concentrations (representing the influence of both hydrological and non-hydrological factors) and flow-adjusted orthophosphate-P concentrations (representing non-hydrological factors only), following Hirsch *et al.*[29] and Jaruskova and Liska.[30] Human related activity may account for a proportion of the latter.[31] For the flow-adjusted analyses, temporal trend analyses were undertaken on residuals obtained from ordinary least squares linear regression of orthophosphate-P concentration *vs.* flow. The data were $\log_{10}$ transformed prior to regression in order to ensure regression residuals were homoscedastic in each of the three cases, although Hirsch *et al.*[29] had previously defended the use of the parametric procedure by stating that it was used only to remove variance explained by the flow variable, rather than using it for statistical modelling *per se*. The significance of all temporal trend results were tested at $\alpha = 0.05$. The Spearman's Rho tests were undertaken using Sigmaplot® 11, while the Mann–Kendall and Seasonal Kendall tests were undertaken using an executable file developed by, and downloaded from, the US Geological Survey.[26] Significance of the correlation coefficients was tested at the $p < 0.05$ level. Autocorrelation function analyses were undertaken using Minitab®17.

The estimation of orthophosphate-P loads (mass per time) reported in the current work are based on the following algorithms:

(i) the quantitation of the low (or base) flow end member load, and its division into a groundwater and an effluent contribution follows the extended end-member mixing analysis (E-EMMA):[3]

$$L_{\mathrm{baseflow}} = L_{\mathrm{effluent}} + L_{\mathrm{groundwater}} \tag{1}$$

$$L_{\mathrm{effluent}} = \Sigma(C_{\mathrm{stw}},\ Q_{\mathrm{dwf\_stw}}) \tag{2}$$

$$L_{\mathrm{groundwater}} = C_{\mathrm{groundwater}} \times Q_{\mathrm{groundwater}} \tag{3}$$

$$Q_{\mathrm{groundwater}} = Q_{\mathrm{river\_min}} - Q_{\mathrm{effluent}} \tag{4}$$

$$Q_{\mathrm{effluent}} = \Sigma Q_{\mathrm{dwf\_stw}} \tag{5}$$

where L is determinand load in g s^{-1}, C is determinand concentration in g m^{-3}, Q is flow in $\mathrm{m}^3\ \mathrm{s}^{-1}$, dwf_stw is sewage treatment work dry weather flow and river_min is the minimum daily mean river flow for the period of interest.

(ii) Method 5 is the favoured OSPARCOM algorithm for estimating determinand loads from periodic concentration and flow data; the load, L, is flow-weighted.[2]

$$L = \left(\frac{K \sum_{i=1}^{n} (Q_i\, C_i)}{\sum_{i=1}^{n} Q_i} \right) \overline{Q} \tag{6}$$

C_i is the deteminand concentration (in g m^{-3}) in each of $i = 1, n$ samples, Q_i is the corresponding daily mean river flow for that sample. K is 86 400 seconds per day and the load L is g d^{-1}. $\bar{Q}$ is the flow-weighted term and is given by:

$$\frac{\sum_{k=1}^{N} Q_k}{N} \tag{7}$$

where Q_k represents daily mean river flows for each day of the year ($k = 1, N$) and N is the number of days in the year.

(iii) Method 3 defined the load as:

$$L = K\sum_{i=1}^{n}\left(C_i\overline{Q}_\mathrm{p}\right) \tag{8}$$

where $\bar{Q}_\mathrm{p}$ is the mean flow for the period between samples.[1]

3. Results and discussion

3.1 Spatial and temporal variability in orthophosphate-P concentrations

3.1.1 Spatial variability. The annual spatial and temporal variability in the concentrations (mean ± one standard deviation) of orthophosphate-P for the R. Taw are summarised in ESI 2.† Concentrations were relatively low in the upper R. Taw at site 11 (generally <0.04 mg P L^{-1}), became markedly higher downstream, 0.089–0.707 mg P L^{-1} at site 9, and then decreased further downstream to 0.036–0.186 mg P L^{-1} at site 2, located close to the tidal limit at site 1. The lower concentrations are typical of rural sites in southwest England showing some evidence of anthropogenic impact.[6,10,11] The elevated concentrations observed at sites 7, 8 and 9 were more typical of urban areas impacted by effluents,[32,33] and were likely to have been due to effluent discharged from the Taw Valley Creamery and STWs located on the upper R. Taw (North Tawton, Belstone/South Tawton; see Fig. 1). Incorporation of effluent orthophosphate-P concentration and flow data from the Creamery and the STWs into a conservative dilution model for the short stretch of river reach between Belstone/South Tawton and Taw Bridge (distance *ca.* 12 km) indicates that the Creamery effluent may have been a significant contributor (up to 100%) to the orthophosphate-P concentration observed at site 7 (Taw Bridge), as shown in Fig. 2. Nevertheless, the STW (population equivalent (pe) 2706) also was important, particularly during the summer.

The annual mean concentration data for orthophosphate-P in tributary rivers are given in ESI 3.† As for the R. Taw, mean concentrations varied by an order of magnitude across the 16 sites, and variations in concentrations about the mean were large at many sites. The relatively high concentrations at site 12, on the R. Mole, were probably due to effluent discharges from the STWs located upstream at South Molton and North Molton; the former is the second largest STW in the catchment and together they have an estimated P load of 2.75 t per year, equivalent to 26% of the STW effluent P loads to rivers across the entire catchment. Downstream of site 12, orthophosphate-P concentrations decreased (sites 13 and 14), presumably due to dilution and/or loss of nutrient from solution. In addition, the tributaries draining into the Mole upstream of site 13, at sites 15 and 16, were low in orthophosphate-P. Sites 19–25 showed wide variability in mean concentrations. In this region there are a number of STWs, with an aggregate pe of over 3000 and an effluent P load of *ca.* 1.4 t per year, and it is likely that these inputs would have contributed to this variability. Lowest mean concentrations occurred at site 18, and at sites 26 and 27 located in the more northerly part of the catchment.

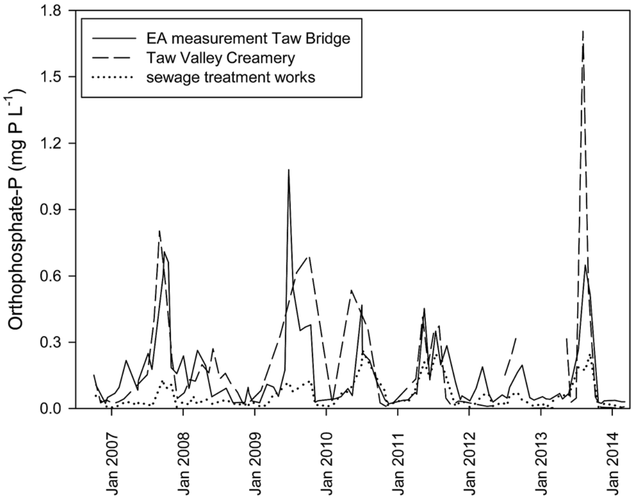


Fig. 2 Estimated concentrations of orthophosphate-P in the river at site 7 (Taw Bridge), between October 2006 and March 2014, due to effluent inputs from the Taw Valley Creamery and the sewage treatment works located on the upper R. Taw. Also shown are the measured concentrations of orthophosphate-P from the EA WIMS dataset for the same period. For the estimated concentrations, orthophosphate-P loads (g P d^{-1}, derived from effluent flow and concentration data) in the effluents were diluted in to the river flow (m^3 d^{-1}) gauged for that day and conservative behaviour of orthophosphate-P assumed.

A decreasing concentration of any dissolved determinand with increasing river flow (the type 1 response[10]) can be largely explained by the dilution of determinand rich effluents or groundwater, or both, with determinand poor diffuse run-off from the catchment. The concentration – flow relationships for orthophosphate-P at sites 2, 7 and 14 exemplify this behaviour (ESI 4(a)†). Recasting the orthophosphate-P data as a monthly time series, shown in ESI 4(b),† similarly reveals that the highest concentrations (and largest standard deviations in concentrations) consistently occurred during the low flow, summer months. Thus, the maximum mean concentrations occurred in September at site 7 (0.94 ± 1.09 mg P L^{-1}), in August at site 2 (0.13 ± 0.09 mg P L^{-1}) and in July at site 14 (0.07 ± 0.05 mg P L^{-1}).

3.1.2 Temporal trends. The results of the temporal trend analyses are reported in Table 2. While the correlation coefficients are weak to moderate (*ca.* −0.3 to −0.5), all three tests show that for each site there was a significant downward trend in orthophosphate-P concentrations over the sampling periods, for both the flow adjusted and non-flow adjusted data. However, the similarity in the magnitude of the correlation coefficients from analyses on the flow adjusted and non-flow adjusted concentrations indicates that hydrological variability may have played a role. There have been changes to river water abstractions and augmentation in the Taw catchment (as noted in Table 1) although it is not possible to attribute any of the changes in orthophosphate-P concentrations to these factors. It

Table 2 Temporal trend analysis of orthophosphate-P concentrations for sites 2, 7 (2003–2013) and 14 (2003–2009)[a]

Site (n)	r_s	Probr_s	Trend	τ	Prob$_{MK}$	Trend	τ	Prob$_{SK}$	Trend
Orthophosphate-P (flow adjusted concentrations)									
2 (126)	−0.32	<0.001	↓	−0.22	<0.001	↓	−0.35	<0.001	↓
7 (129)	−0.42	<0.001	↓	−0.28	<0.001	↓	−0.32	<0.001	↓
14 (83)	−0.37	<0.001	↓	−0.22	<0.001	↓	−0.30	0.007	↓
Orthophosphate-P (non-flow adjusted concentrations)									
2 (126)	−0.32	<0.001	↓	−0.22	<0.001	↓	−0.36	<0.001	↓
7 (129)	−0.35	<0.001	↓	−0.23	<0.001	↓	−0.37	<0.001	↓
14 (83)	−0.40	<0.001	↓	−0.26	<0.001	↓	−0.47	<0.001	↓

[a] n, number of data points; r_s, Spearman's Rho correlation coefficient; τ, Kendall's tau correlation coefficient; Prob, p value of the significance of the trend; r_s, Spearman's Rho; MK, Mann Kendall; SK, Seasonal Kendall.

has been shown that median (Q_{50}) flows during the summer and autumn (June–November) for the period 1969–2008 increased by 10–30% in the southwest of England, probably due to climatic factors.[34] In principle, increased river flows during summer and autumn would, *inter alia*, lead to increased dilution of the point source orthophosphate-P loads that tend to dominate during these periods, and hence give rise to lower river orthophosphate-P concentrations. This may explain, to some extent, why the Seasonal Kendall test returns larger positive correlations in each case than the Mann Kendall test, which doesn't explicitly account for seasonal scale changes in the data (Table 2). However, this hypothetical scenario is likely to be confounded by the complexity of catchment nutrient cycling, sources and losses, and their changes with time. Recent decreases in orthophosphate-P concentrations observed in English rivers in the last decade or so have been due to nutrient stripping of STW effluents prior to final discharge.[7,10,35,36] In the Taw catchment, orthophosphate-P stripping has not been implemented under the UWWTD because of the relatively small sizes of the individual STWs within the catchment, and so the downward trends in orthophosphate-P concentrations cannot be ascribed to this driver. Reductions in P-loading of domestic detergents may have played a role,[37] but as temporal trend data for effluent P loads from STW in the catchment were not available, this suggestion is tentative. The downward trend may also be explained, in part, by changes in P_2O_5 fertiliser applications over the last decade; for grassland in southwest England, applications have decreased by *ca.* 30% since 2002, to 7 kg ha^{-1} P in 2013, while for all crops and grass the inputs have halved over the same period to 14 kg ha^{-1} P in 2013.[38,39] An additional factor that could generate an apparent trend in decreasing orthophosphate-P concentrations is a change to lower resolution sampling and subsequent flattening of the signal.[40–42] In the current study, the apparent downward trends in concentrations observed from the early-2000s was not accompanied by a clear change in sampling frequency, and so the trends, if real, were due to factors that are unidentified at present. The potential consequences for improved ecological status of these apparent reductions in orthophosphate-P concentrations, in relation to phytoplankton growth and community composition, are examined in Section 3.3.

3.2 Orthophosphate-P sources and loads

3.2.1 Catchment integrated diffuse sources. The approximately asymptotic decrease in orthophosphate-P concentrations as flows increased, described in Section 3.1.1, can provide information on the integrated diffuse (run-off from the surface and unsaturated zone that could include agricultural and septic tank sources[35,43]) orthophosphate-P contribution from the catchment to the river. A quantitative estimate of this contribution can be derived from the gradient of the regression of orthophosphate-P load *vs.* flow.[43,44] The underlying assumption of this approach is that an increase in orthophosphate-P load is due only to this diffuse term, while loads from other important sources (groundwater and STW/industrial effluent) remain uniform regardless of overall river flows.[9,44] We do not have the data to test this assumption however, as is outlined in Section 3.2.2. In the current work, concentration and flow data for all years at each site have been used for the quantitation because annual sampling frequency was generally low (10–13 samples per year). Thus, the results reflect an integration of all the spatial and temporal variation in inputs across the catchment plus any in-water orthophosphate-P gain/loss that may have occurred (*e.g.*[43]). In an earlier study[44] ordinary least squares regression (OLS) was used to quantify the relationship between load and flow. However, in the current work a robust linear regression (bisquare weight method) has been used to quantify the relationship as this technique is less sensitive than OLS to heteroscedasticity in the data and the presence of outliers.[45] The results of the regression analyses are reported in ESI 4(c)† for sites 2 and 14 which represent the riverine outlets from the Taw and Mole sub-catchments. The relationships between load and flow at both sites are significantly ($p < 0.001$) and positively linearly correlated, with R^2 values of 0.93 and 0.95, respectively. The slopes of the lines indicate that the Taw and Mole sub-catchment contributions to orthophosphate-P concentrations were of the order 0.035 mg P L^{-1} (0.034–0.036 mg P L^{-1}, 95% CI) and 0.019 mg P L^{-1} (0.018–0.021 mg P L^{-1}, 95% CI), respectively. In order to reveal variability around these 1990–2013 integrated values, separate regressions between load and flow were undertaken for site 2 for 1991 to 1996 when sampling was more frequent (25–35 samples per year). In all cases the R^2 values were strongly positive (range 0.75–0.94) and slope values (mean 0.054 mg P L^{-1} and range 0.029–0.076 mg P L^{-1}) similar to or higher than the concentration shown in ESI 4(c).† It is noteworthy that the reported year on year reductions in fertiliser P loads have not obviously influenced the catchment integrated diffuse loads of orthophosphate-P. This de-coupling, if real, may simply be a reflection of complexity in the mobilisation and transfer of phosphorus at large areal scales.[46] The diffuse catchment concentrations estimated here are similar to those observed for the rural R. Tamar catchment (southwest England) (range 0.025–0.118 mg P L^{-1}) but lower than those calculated for the urbanised R. Thames and R. Thame catchments (southeast England) (range 0.097–0.298 mg P L^{-1}).[11,36]

The approximately conservative behaviour of orthophosphate-P evidenced by the positive and significant coefficients of determination in the load *vs.* flow plots in ESI 4(c)† is perhaps counter-intuitive given the multitude of orthophosphate-P sources across the catchment, the downward temporal trend in river orthophosphate-P concentrations and known *in situ* orthophosphate-P reactivity in rivers.[3,43] With respect to *in situ* reactivity, exchange of phosphorus between river bed sediments, pore waters and overlying waters in the upper Taw river and tributaries has been reported to be limited.[47] In addition, within-river P cycling was unimportant relative to the source loadings of orthophosphate-P in the Dorset R. Frome, located in southern England.[9] A more rigorous assessment of orthophosphate-P behaviour (*i.e.* conservative, non-conservative) is desirable, but this would require higher temporal sampling resolutions (daily, weekly) than the monthly sampling adopted by the EA.[3]

3.2.2 Sources and loads at river base flow.

Eqn (1)–(5), given in Section 2.3, were used to quantify the low (or base) flow end member loads of orthophosphate-P from groundwater and effluent. There are no direct measurements of groundwater orthophosphate-P concentrations in the Taw catchment, but typical concentrations of total dissolved phosphorus (orthophosphate-P + refractory inorganic P + organic P) in a wide range of English groundwaters, including from the nearby Dartmoor granite, are <0.1 mg P L^{-1}.[48,49] Incorporation of the groundwater (0.1 mg P L^{-1} used for concentration) and STW flow and concentration data into eqn (1)–(5) revealed that STW effluent could theoretically contribute 96%, 85% and 72% of the orthophosphate-P load at site 7 (the Creamery effluent was included for this site; median P concentration is 5.5 mg L^{-1}), site 2 and site 14, respectively, during lowest river flows. The estimated dominance of the effluent signal at site 7 is in good agreement with the results from the dilution model assessment shown in Fig. 2. From this perspective, *i.e.* the dominance of effluent orthophosphate-P at low river flows, the Taw is typical of rivers across the UK.[10,13,35,36,43,44]

3.2.3 A source apportionment model for orthophosphate-P.

The catchment integrated diffuse source concentrations of orthophosphate-P reported in Section 3.2.1 were combined with the orthophosphate-P loads from effluents and groundwater calculated in Section 3.2.2 to give a source apportionment model (SAM) that is analogous to the Type 1 E-EMMA described in Jarvie *et al.*[3] This three end-member load mixing model can calculate the contribution of each source (effluent, groundwater, catchment) to the overall orthophosphate-P load as river flow increases. As such, the SAM can be viewed as an initial, pragmatic, attempt to examine the relative importance of orthophosphate-P loads under contrasting flow regimes, and provides a basis for more detailed studies of orthophosphate-P loads if or when higher temporal resolution orthophosphate-P concentration data become available. In the SAM the same assumption was made regarding changes in load as given in Section 3.2.1, that only the diffuse loads increased with flow (thus for each 1 $m^3\ s^{-1}$ increase in flow the diffuse load would increase by 0.035 g P s^{-1} and 0.019 g P s^{-1} for the Taw and Mole sub-catchments, respectively). The results from the SAM are given in Fig. 3. At the lowest flows, effluent loads dominate (72–85%) at the outlets of the Taw and Mole sub-catchments (consistent with the loads estimated using eqn (1)–(5), while groundwaters contribute 15–28%. At the highest river flows, in contrast, diffuse loads dominate (91–93%) and effluent loads are only *ca.* 6% of the total. Nevertheless, effluent orthophosphate-P contributes ≥50% of load for approximately a half and a quarter of the time in the Taw and Mole, respectively; which again emphasises the importance of effluent orthophosphate-P during the critical low-flow, algal growing season.

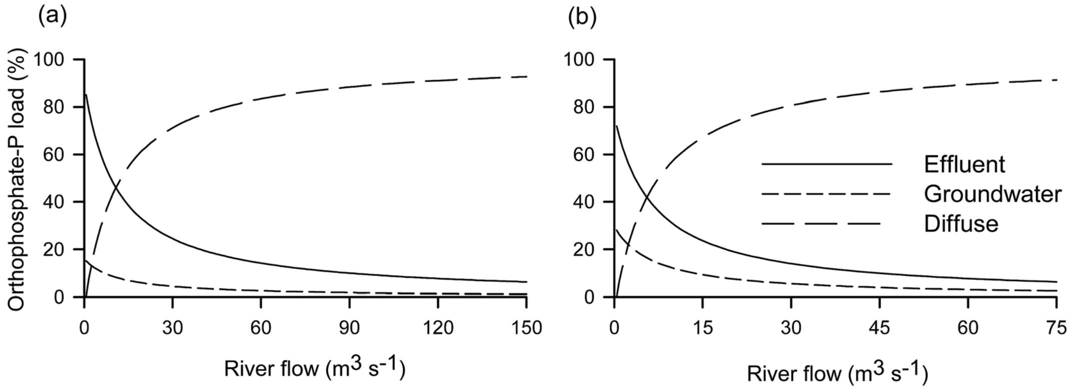


Fig. 3 Calculated orthophosphate-P load from effluent, groundwater and diffuse run-off (%) *vs.* river flow ($m^3\ s^{-1}$) at (a) site 2 on the R. Taw and (b) site 14 on the R. Mole. Note changes in scales.

3.2.4 Loads derived from EA WIMS data. Orthophosphate-P loads at each of the gauged sites were also calculated directly from river flow and EA WIMS monitoring data for the days for which orthophosphate-P data were available. Concentrations given as less than (these were $\ll$1% of the total dataset) were divided by 2 for the calculation.[50] The favoured OSPARCOM approach for load estimation was used[2] (the flow weighted Method 5, eqn (6) in Section 2.3). Mean and median daily load values were then calculated for each year, and the results are shown in Fig. 4(a). In each case the mean loads were similar to or larger than the median loads; the largest differences were observed at site 7, presumably because of the occurrence of enhanced orthophosphate-P concentrations at this site (ESI 2†). Highest mean loads were observed at site 2 and were in the range 34–191 kg P d^{-1}, reflecting the relatively large size of its drainage area and hence river flows. The next highest loads occurred at site 7 (12–116 kg P d^{-1}). Loads from site 14 on the R. Mole were in the range 20–60 kg P d^{-1} and showed much less annual variation than the R. Taw sites. The magnitude of the loads decreased in the latter half of the time series, a trend that is consistent with the reduction in concentrations described in Section 3.1.2. The trend of decreasing loads is particularly marked at site 7 in the upper R. Taw and site 14 on the R. Mole.

Bowes *et al.*[40] calculated loads of SRP in the high BFI (0.84) R. Frome (southern England) using an algorithm assessed to be the most accurate (lowest bias) and least imprecise (Method 3, eqn (8) in Section 2.3). Based on monthly sampling, bias in annual load estimates for SRP in the R. Frome were in the range −10.6 to +12.2% (with one at +27.9%) relative to the 'true' load calculated from more frequently collected samples (average 3.7 samples per day for one year). Load bias may be greater in the Taw because it is a lower BFI (0.43) catchment, although because it also has a low population density, this may not necessarily be the case.[41] Load estimates for total reactive phosphorus (equivalent to orthophosphate-P in the current work) based on EA monitoring data (6 samples per year; May 2011–September 2012), and using the Method 5 algorithm, gave a bias of +7.1% compared with higher resolution (hourly) data, in the low BFI (<0.50) R. Leith (northwest England) catchment.[51] However, loads calculated during periods dominated by either low or high river flows showed much poorer agreement with the high sample resolution based loads, implying, *inter alia*, that the data record timespan used for inter-comparisons is important. Indeed, it has been shown that high resolution sampling is necessary in order to quantify short term variability in orthophosphate-P concentrations and hence loads.[40] From these studies it can be concluded that the load estimates given in the current work may have a bias of up to ±20%. Maier *et al.*[52] reported the average orthophosphate-P load at Umberleigh (site 3 in the current study) to be 37 t per year for the period 1990–2004. Extrapolation of our estimates at site 2 to an annual basis gives an average of 44 t per year over the same period and 38 t per year over the longer period of 1990–2013 examined herein, both of which are within the bias error given above.

A comparison of the loads derived from the EA WIMS monitoring data and the SAM was undertaken for sites 2 and 14. The EA derived mean and median loads for each year were plotted against the mean river flow for the year (the latter calculated from the flow weighted Method 5) and compared against the SAM calculated loads for the same flow range; the results are presented in Fig. 4(b). While the SAM calculated loads increase monotonically with flow (because only river flow changes in the model) they fall centrally within the ranges calculated using Method 5 for both sites. This agreement

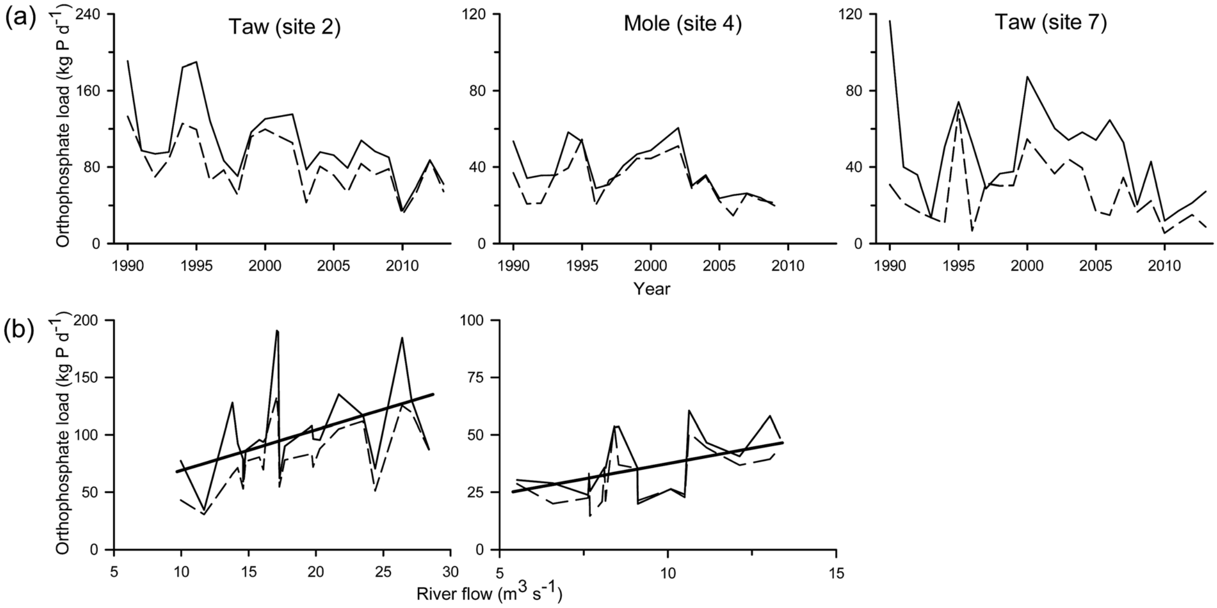


Fig. 4 (a) Orthophosphate-P load (kg P d^{-1}) for each year and (b) orthophosphate-P load (kg P d^{-1}) *vs.* annual mean flow (m^3 s^{-1}) for each year at three sites on the R. Taw and R. Mole. Note changes in scales. Thin solid line, Method 5 mean value; dashed line, Method 5 median value; thick solid line, source apportionment model value.

indicates that the inclusion of temporally variable orthophosphate-P loads into the SAM would improve the correlation between these two load estimation approaches. Diffuse load data for orthophosphate-P at site 2 (*cf.* ESI 4(c)†) were calculated separately for the years 1991 to 1996 when sampling frequency was relatively high (25–35 samples per year), and the modelled loads recalculated for each of those years (<8% of the data used to calculate the diffuse values were excluded as outliers). Subsequent bisquare weight linear regression of EA derived median loads against SAM calculated loads gave an R^2 of 0.91 and a slope of 1.23 ($n = 5$, 1995 excluded). Although n is small, this good fit indicates that the approach used for estimating the diffuse concentration, exemplified in ESI 4(c),† is robust and that, on an annual basis, the estimated loads calculated by the two methods are not likely to be significantly different given that the bias (23%) is of a similar order to the bias in orthophosphate-P load estimations reported previously.[40,51] While this agreement is encouraging, the advantage of the SAM approach, relative to the Method 5 load estimation, is the ability to separately identify the diffuse and point load components.

The load estimation approaches described in Sections 3.2.1 to 3.2.4 can be summarised and linked in the following way. Base flow orthophosphate-P loads from groundwater and effluents revealed that at lowest river flows, effluent contributed 72–96% of the load at the three sites examined. Data from the base flow loads and integrated catchment inputs of orthophosphate-P were combined to give a source apportionment model which showed that effluent orthophosphate-P contributed at least half of the orthophosphate-P load for 27–48% of the time. This outcome is consistent with recent reports of the importance of effluent orthophosphate-P at low river flows in other English catchments (*e.g.*[10]). Orthophosphate-P loads were also calculated from EA WIMS data using the OSPARCOM Method 5 and compared with the loads derived from the SAM. The proximity between the load estimates derived from the two approaches appeared to be of the same magnitude as the bias in orthophosphate-P loads reported for other lower BFI English rivers.[51] It is anticipated that inclusion of more highly temporally resolved data would improve the agreement between these two load estimation approaches, although there appears to be a dearth of studies on the relationship between sampling frequency and orthophosphate-P load uncertainties in effluent impacted low BFI UK rivers.

3.3 Water quality

3.3.1 Water Framework Directive Phase 2 standards for reactive phosphorus. Site specific standards for reactive phosphorus (RP) under Phase 2 of the WFD standard setting process were implemented in 2015.[16,53] In Phase 2, RP is defined as phosphorus that will pass through a 0.45 μm pore size filter membrane and can be measured by the phosphomolybdenum blue colourimetric method.

The RP standard, which is a calculated annual mean concentration, is defined by eqn (9):

$$\text{RP standard } (\mu\text{g P L}^{-1}) = 10\text{\^{}}((1.0497\log_{10}(\text{EQR}) + 1.066) \times (\log_{10}(\text{reference condition RP}) - \log_{10}(3500)) + \log_{10}(3500)) \quad (9)$$

The RP standard is the concentration estimated for the lower class boundary of the High, Good, Moderate and Poor Ecological Status. The Ecological Status depends on the value of EQR used, where EQR is the site independent ecological quality ratio

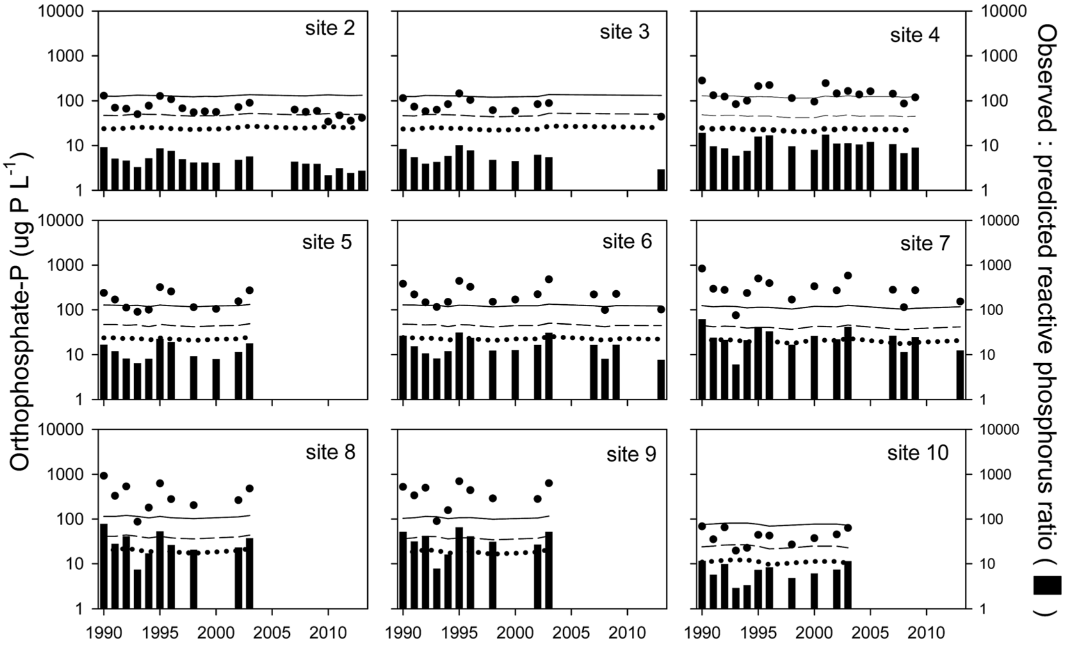


Fig. 5 Water framework directive (Phase 2) reactive phosphorus standards for the R. Taw. Solid line, poor/moderate boundary; dashed line, moderate/good boundary; dotted line, good/high boundary (all μg P L^{-1}). Observed mean annual concentrations of orthophosphate-P (●; μg P L^{-1}). Vertical bars show the ratio of the observed and predicted reactive phosphorus concentrations.

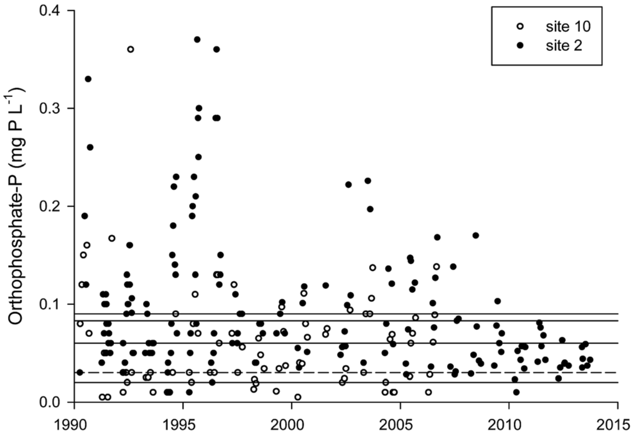


Fig. 6 Orthophosphate-P (mg P L^{-1}) concentrations at site 10 and site 2 on the R. Taw during the April to September algal growing period. The horizontal lines show the Phosphorus Limiting Concentrations (PLC), reported for different UK and US rivers, below which P was the limiting nutrient and periphyton growth declined. The dashed line shows the concentration below which a positive change in diatom community composition was observed. See Bowes *et al.*[54] for a more detailed account of the PLC data.

at the class boundary.[15,16] The 'reference condition RP' is the RP concentration expected at near natural conditions, subject to local geology and geography. It can be estimated as:

$$\text{Reference condition RP} = 10\hat{}(0.454(\log_{10}\text{alkalinity}) - 0.0018(\text{altitude}) + 0.476) \quad (10)$$

Alkalinity is the mean annual total alkalinity (mg $CaCO_3$ L^{-1}) of the water (a proxy for geology and location) at a given site and the altitude is height (in m, AOD). The annual spatial and temporal variability in the concentrations (mean ± one standard deviation) of alkalinity for the R. Taw and the tributary rivers are summarised in ESI 5 and 6,† respectively. There were no clear temporal trends in mean annual concentrations of alkalinity across the catchment, but there were marked spatial differences. On the R. Taw there was a notable increase in alkalinity concentrations in the upper catchment between site 10 and the downstream site 9. This pattern, and indeed the trends in the remainder of the R. Taw, mirrored those of orthophosphate – P. In the tributary rivers, the highest mean concentrations occurred at sites 22–25 and to a lesser extent at sites 19–21. It is also noteworthy that the sites with the highest mean concentrations also had the largest standard deviations about the mean concentration.

Eqn (9) and (10) have been used to retrospectively examine the compliance of the R. Taw and its tributaries with the Phase 2 RP standards and the results are reported in Fig. 5 and ESI 7.† For the R. Taw itself, most sites (4, 5, 6, 7, 8, 9) would be classified as 'Poor', while sites 2, 3 and 10 would be classified as 'Moderate' and site 10 occasionally as 'Good'. The ratio of the measured RP to reference condition RP can be calculated for each year for each site and is a quantitation of the human impact on ambient phosphate-P concentrations.[15] The ratio values reflect the range found for Ecological Status, with measured orthophosphate-P concentrations at 'Poor' sites factors of 10 or more above the reference condition, implying marked anthropogenic nutrient pressures at these locations. For the tributary rivers the Ecological Status would be better, with a number of sites achieving 'Good' in some years (sites 14, 15, 16, 18, 26, 27). Nevertheless, sites 19–25 appear particularly impacted, with a 'Poor' status dominant and ratios generally >10.

While there are uncertainties in correlating RP standards with actual biological impacts,[16] it is likely that concentrations

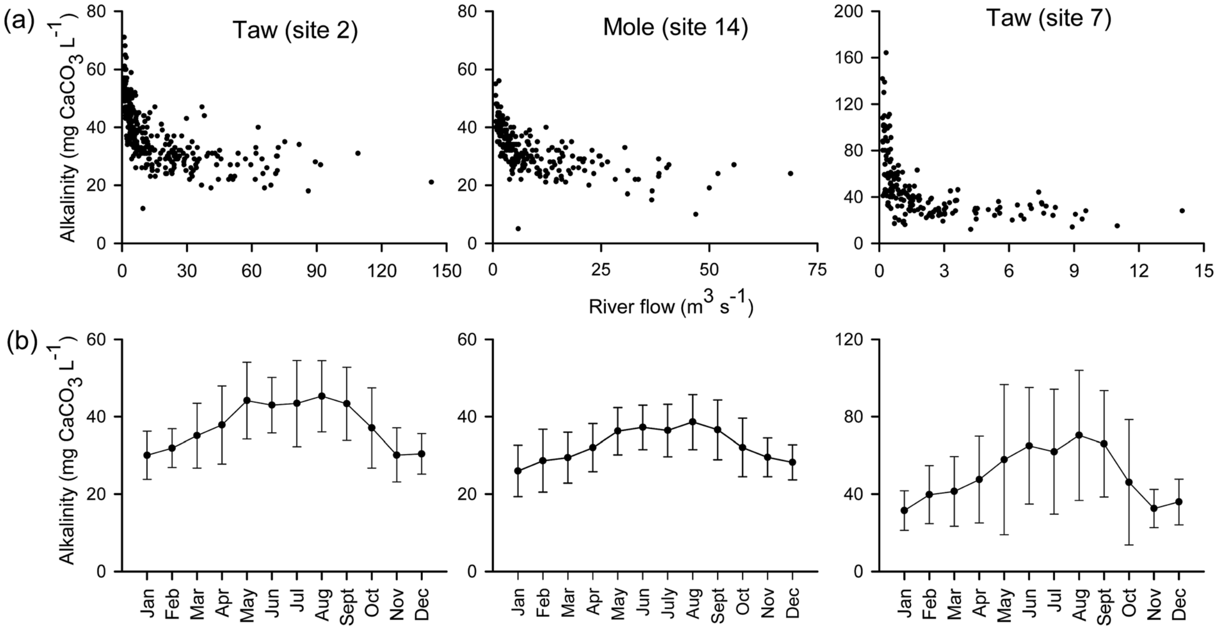
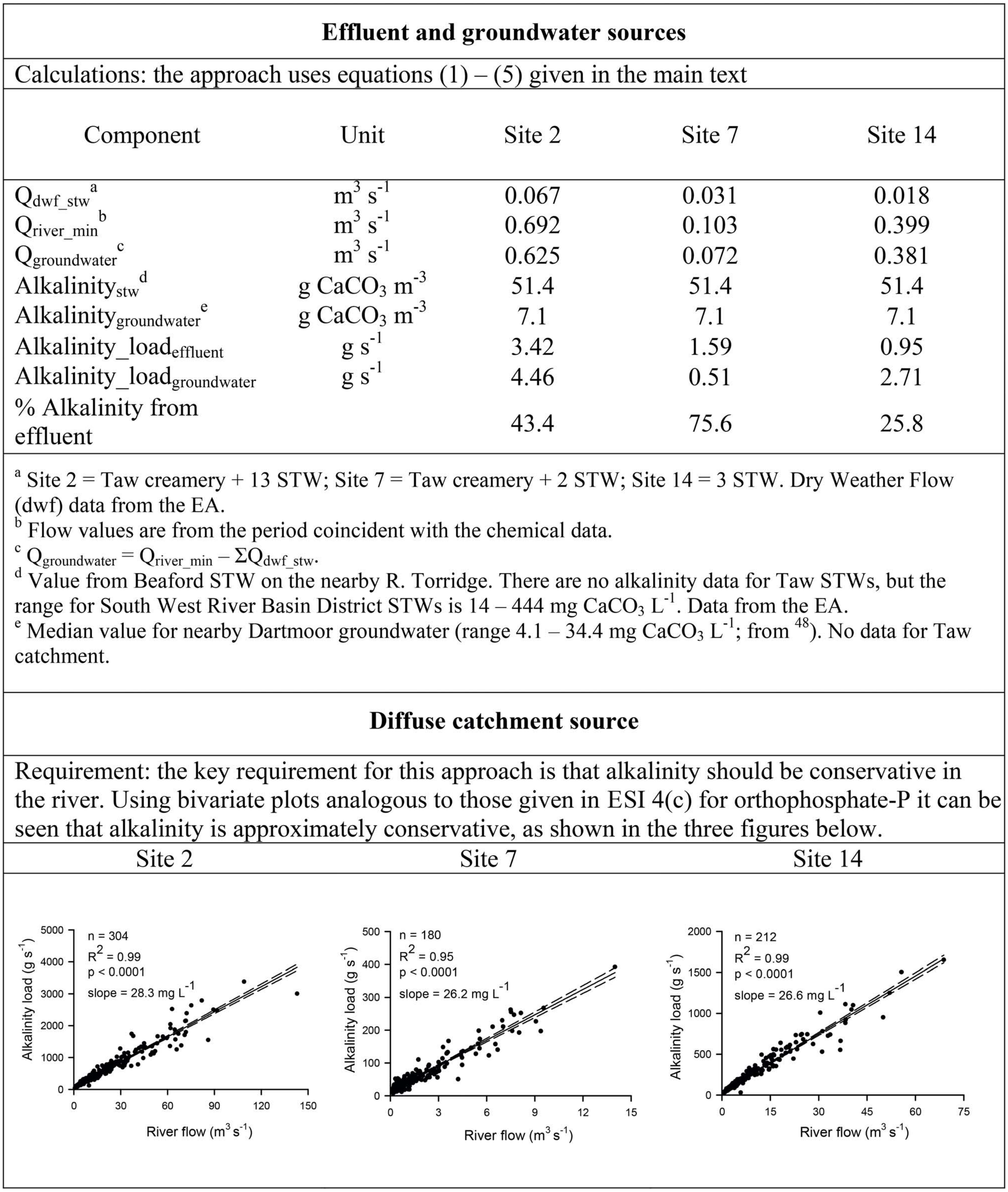


Fig. 7 (a) Concentrations of total alkalinity (mg $CaCO_3$ L^{-1}) *vs.* river flow (m^3 s^{-1}) at gauged sites on the R. Taw and R. Mole. (b) Monthly mean (±1 standard deviation) concentrations of total alkalinity (mg $CaCO_3$ L^{-1}) for the same sites. Note changes in concentration scales.

of orthophosphate-P in the Taw catchment rivers, particularly during summer, were generally above concentrations considered detrimental to periphyton and benthic diatom communities. Fig. 6 shows orthophosphate-P concentrations for the summer growing season (April to September) for two sites on the Taw with the lowest orthophosphate-P values; site 10 in the upper catchment and site 2 at the catchment outlet (for the tributaries, only sites 18, 26 and 27 exhibited similarly low concentrations). Also shown on Fig. 6 are reported Phosphorus Limiting Concentrations (PLC) for some UK and US rivers below



Effluent and groundwater sources

Calculations: the approach uses equations (1) – (5) given in the main text

Component	Unit	Site 2	Site 7	Site 14
Q_{dwf_stw} [a]	$m^3\ s^{-1}$	0.067	0.031	0.018
Q_{river_min} [b]	$m^3\ s^{-1}$	0.692	0.103	0.399
$Q_{groundwater}$ [c]	$m^3\ s^{-1}$	0.625	0.072	0.381
$Alkalinity_{stw}$ [d]	$g\ CaCO_3\ m^{-3}$	51.4	51.4	51.4
$Alkalinity_{groundwater}$ [e]	$g\ CaCO_3\ m^{-3}$	7.1	7.1	7.1
$Alkalinity\_load_{effluent}$	$g\ s^{-1}$	3.42	1.59	0.95
$Alkalinity\_load_{groundwater}$	$g\ s^{-1}$	4.46	0.51	2.71
% Alkalinity from effluent		43.4	75.6	25.8

[a] Site 2 = Taw creamery + 13 STW; Site 7 = Taw creamery + 2 STW; Site 14 = 3 STW. Dry Weather Flow (dwf) data from the EA.

[b] Flow values are from the period coincident with the chemical data.

[c] $Q_{groundwater} = Q_{river\_min} - \Sigma Q_{dwf\_stw}$.

[d] Value from Beaford STW on the nearby R. Torridge. There are no alkalinity data for Taw STWs, but the range for South West River Basin District STWs is 14 – 444 mg $CaCO_3\ L^{-1}$. Data from the EA.

[e] Median value for nearby Dartmoor groundwater (range 4.1 – 34.4 mg $CaCO_3\ L^{-1}$; from [48]). No data for Taw catchment.

Diffuse catchment source

Requirement: the key requirement for this approach is that alkalinity should be conservative in the river. Using bivariate plots analogous to those given in ESI 4(c) for orthophosphate-P it can be seen that alkalinity is approximately conservative, as shown in the three figures below.

Site 2 Site 7 Site 14

Fig. 8 Estimation of the contribution of effluents, groundwater and diffuse catchment sources to river alkalinity loads at sites 2, 7 and 14 in the Taw catchment.

which periphyton biomass accrual rates were observed to decline (summarised in[54]). It can be seen that most orthophosphate-P concentrations were in the range of these PLC values, particularly in the later part of the time series. Targeted experiments on the Taw itself would be required to see if a decrease in algal biomass had indeed occurred. As these sites probably represent the best case scenarios it is likely that the remaining sites in the Taw catchment would require more comprehensive mitigation measures in order to achieve GES with respect to orthophosphate-P.

3.3.2 Does the use of alkalinity compromise the phosphorus standards?

Within the WFD Phase 2, the phosphorus-P standards for rivers are dependent on alkalinity and altitude, as described above. In the unperturbed, or 'reference' sites of Phase 2, alkalinity and altitude explain most of the variation in river RP concentrations because these parameters "take into account the main sources and controls of the natural variation in soluble phosphate concentrations (*i.e.* rock weathering)".[15] Thus the reference conditions are defined by an absence of anthropogenic pressures and indicate that river flows are driven by natural catchment hydrology. The resulting linear regression of alkalinity/altitude with RP is used to calculate the 'expected' concentration of RP at any site in the UK. This value is also used to determine the RP concentrations that delineate the boundaries between the five different Ecological Status classifications, as described in Section 3.3.1.

While the Phase 2 RP standards are framed as annual mean concentrations, many studies have highlighted the importance of orthophosphate-P to periphyton and benthic diatom growth during the low flow, summer months.[13,55] From eqn (1) it has been established that low river flows can have contributions from both groundwater and effluents from sewage treatment and industrial sources, and the relative importance of these sources to orthophosphate-P at three sites in the Taw was estimated from eqn (1)–(5). This approach can be extended to alkalinity because sewage (and some industrial) effluent contains alkalinity (principally carbonate/bicarbonate, but also borate and organic acids, and orthophosphate-P itself[18]), and so, at low flows, riverine alkalinity will have both a groundwater and an effluent component. Summary plots of alkalinity concentration *vs.* river flow and monthly variations in alkalinity concentrations for the sites 2, 7 and 14 in the Taw catchment (Fig. 7(a) and (b), respectively) are consistent with this contention, with the highest concentrations occurring at low flows and during the summer months. Notably, these trends mirror those for orthophosphate-P shown in ESI 4(a) and (b).†

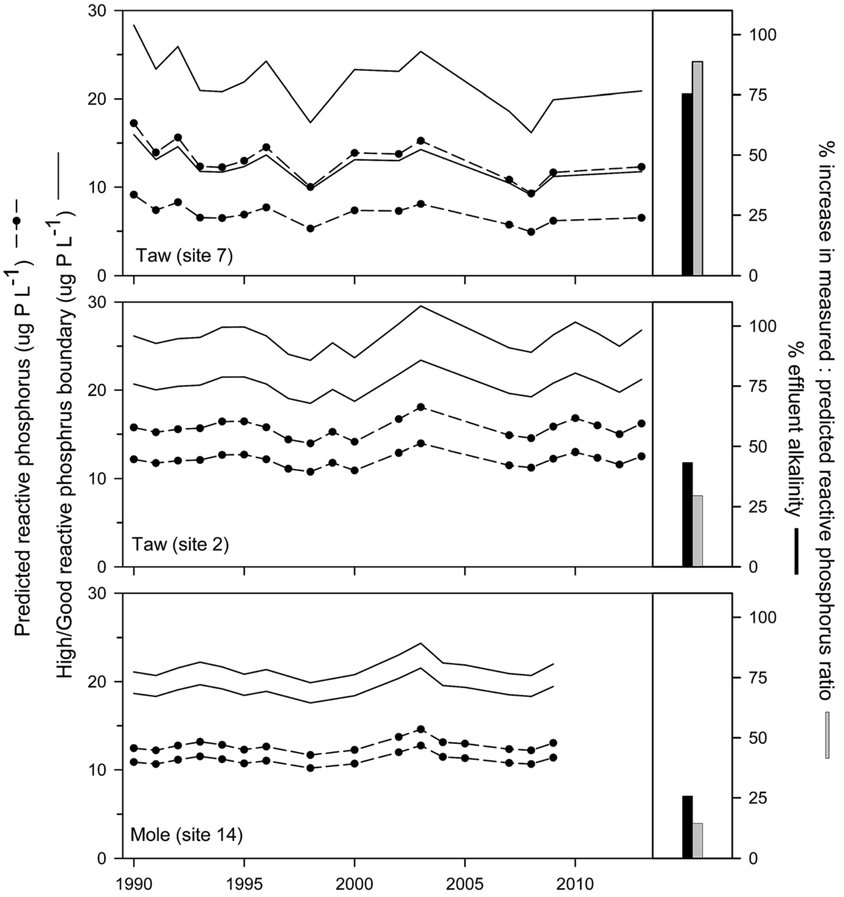


Fig. 9 Right panel: bar chart shows the % contribution of effluent to the measured river alkalinity at each site and the % increase in the measured: predicted reactive phosphorus (RP) ratio after subtraction of the effluent component of the measured alkalinity. Left panel: Solid lines show the decrease in the High/Good boundary concentration of RP, while the circle/dashed lines show the decrease in the predicted RP concentration, after subtraction of the effluent component of the measured alkalinity. Analysis for the summer period (April–September) only.

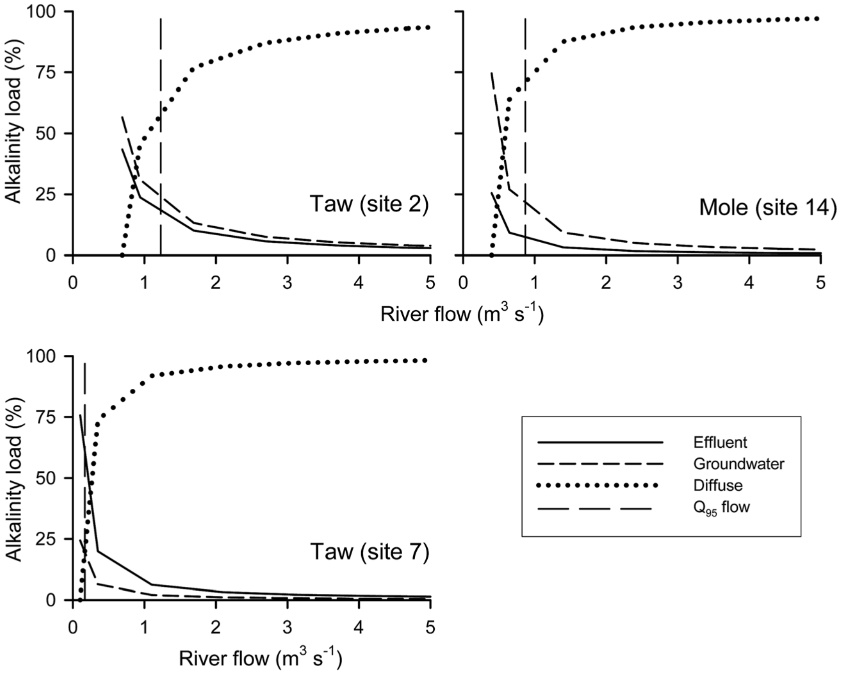


Fig. 10 Estimated contribution to river alkalinity load from effluent, groundwater and diffuse run-off (%) *vs.* river flow ($m^3\ s^{-1}$) at three sites on the R. Taw and R. Mole. The Q_{95} flow values are from Table 1.

The presence of effluent alkalinity implies that the calculated "reference condition" and "Ecological Status boundary" RP concentrations may be incorrect, the size of the discrepancy being dependent on the proportion of effluent alkalinity. In addition, the calculated RP concentration at a given boundary may be higher in effluent influenced rivers, relative to groundwater dominated rivers, thereby giving a misleading impression of the ecological status of the water body. Separation of the measured alkalinity at low river flows into these two components, using eqn (1)–(5), has been done for sites 2, 7 and 14. Fig. 8 summarises the calculations, including the data used and underlying assumption made. Thus, it has been estimated that *ca.* 43, 76 and 26%, respectively, of the measured river alkalinity at these sites was from effluent. Reference condition RP and High/Good RP boundaries were then calculated with and without this effluent component for the ecologically important summer period of April to September (Fig. 9). The measured: predicted RP ratio increased by 29%, 89% and 15% at sites 2, 7 and 14, respectively, while the reference condition RP concentrations decreased by the same margins. The associated RP concentrations delineating the High/Good boundary fell by 26%, 78% and 13%, respectively, at these sites.

The significance of these results with respect to nutrient reduction strategies, at this time, should be placed in the context that the Phase 2 standards are for annual mean concentrations of both alkalinity and RP. For example, using the data in Fig. 8, it is possible to apportion river loads of alkalinity from the different sources (effluent, groundwater, diffuse) against changes in river flow (*cf.* orthophosphate-P in Fig. 3). The results, shown in Fig. 10, suggest that both effluent and groundwater alkalinity are important at low flows, consistent with the calculations above. Thus, for flows $\leq Q_{95}$ value, effluents may account for 25–50% of the alkalinity load for the sites representing the outlets of the Taw and Mole catchments. Nevertheless, because of the paucity of data on flows and concentrations used in this analysis, as noted in footnotes d and e to Fig. 8, these results probably provide only a first order assessment of the importance of alkalinity sources under contrasting river flows, and in particular at low flows. Additional work using more constrained datasets would serve to reduce the uncertainties and arguably contribute to a more refined set of phosphorus standards for inclusion in a Phase 3 cycle of standards revisions under the WFD.

4. Summary and conclusions

The results from a source apportionment model incorporating effluent, groundwater and diffuse loads of orthophosphate-P suggested that effluent discharged to the rivers in the Taw catchment contributes approximately half of the orthophosphate-P load for up to half of the time across the catchment. However, during the more biologically important summer months, significant contributions of sewage (across the catchment) and industrial effluent (upper R. Taw) to orthophosphate-P concentrations (up to 96%) occur. These sources probably contribute to the generally Poor to Moderate Ecological Status of the rivers with respect to the recently introduced WFD Phase 2 standards for phosphorus. Since the early-2000s, orthophosphate-P concentrations appear to have decreased, for reasons not identified herein, with no clear improvement in overall ecological status. To compound the failure to meet Good Ecological Status at most sites sampled, it has been demonstrated that sewage and industrial effluent sources of alkalinity to the river can give erroneous boundary concentrations of reactive phosphorus for WFD Ecological Status classification, and in effect relax the standards.

While the sampling resolution of the EA chemical monitoring programme, particularly in the temporal dimension, frequently attracts criticism, the resulting data archived in the WIMS database, at a national level, are an important resource that can be used, with due diligence, to assess and address problems in catchment management. In the current work, the high orthophosphate-P concentrations observed in the upper R. Taw were largely due to industrial effluent from a single source, coupled with more minor contributions from STWs, while at the catchment scale, the enhanced summer concentrations of orthophosphate-P were due to STW effluents. These point sources appeared to be the major cause of failure to meet GES under the WFD. Reductions in orthophosphate-P loads from effluents could be achieved *via* chemical precipitation using metal chloride, although the costs may be prohibitive. In the future, the development of an EU-wide Phosphorus Circular Economy to severely restrict P losses to the environment, as advocated by the European Sustainable Phosphorus Platform, may drive through these mitigation measures. The estimated diffuse catchment runoff concentrations of *ca.* 0.03 mg L^{-1} orthophosphate-P, if maintained at this level, would alone cause many sites to fail GES under the WFD Phase 2 standards. There is no requirement under the current UWWTD to further reduce orthophosphate-P loads from STW and industrial effluents in the Taw catchment and so unless driven by the WFD, it is unlikely that most rivers in the Taw catchment will achieve GES in the foreseeable future.

For catchments like the Taw, with an extensive sampling history, both spatially and temporally, it is arguable that the regulatory agencies should investigate alternative sampling strategies that would provide more useful data for management/policy purposes while at the same time be resource neutral and still fulfil statutory monitoring obligations. For example, the number of sites regularly sampled could be reduced to those with known issues plus sites located at the catchment outlets, including sub-catchments, where sampling frequency could be markedly increased. The latter approach would provide improved estimates of catchment nutrient loads, as defined in this study, and at the same time allow more accurate and precise land to sea flux estimates of contaminants required by OSPARCOM. Reduced routine sample throughput could also allow a more comprehensive set of analyses per sample, of particular importance for phosphorus because it occurs in a variety of inorganic and organic fractions with varying bioavailabilities. With anticipated changes in rainfall patterns, in particular increases in the frequency of short sharp summer rain events, it may be prudent to undertake "smart sampling" during these events (using a combination of meteorological predictions for summer rainfall with *in situ* measurement technologies) in order to improve understanding of nutrient transfers during intermittent wetting up of catchments. The aspiration for *in situ* measurements, *inter alia*, is that they should measure the bioavailable P as defined by the Environmental Quality Standard that is current at the time; while *in situ* measurements of (dissolved) reactive phosphorus in rivers are now being more frequently reported, it is evident that the instrumentation requires further development, particularly in relation to the more specific definition of filtered reactive phosphorus given in the WFD Phase 2 standard.

The contribution of sewage effluent to riverine concentrations of alkalinity appeared significant in the Taw, particularly during the key summer months. Given the extent of urbanisation within Europe it would appear prudent to extend this analysis in order to properly assess the contributions of effluent alkalinity to river alkalinity across the EU. This would no doubt provide a more nuanced derivation of river phosphorus standards in a future WFD river basin management cycle.

Abbreviations and definitions

Term	Abbreviation	Definition
Above ordnance datum	AOD	Height (in m) above mean sea level at Newlyn
Base flow index	BFI	Generally, the contribution of groundwater flow to river runoff as a ratio; the higher the contribution the higher the BFI value
Daily mean flow	DMF	Mean river flow (in $m^3 s^{-1}$) in a water-day (09.00 to 09.00 GMT). Typically, flows are calculated on the basis of measurements at 15 minute intervals
Extended end-member mixing analysis	E-EMMA	The use of water quality monitoring data to generate plots of flux of a chemical analyte against flow which may be used to infer and quantify analyte retention and/or release within a river catchment
Ecological quality ratio	EQR	This determines the P concentration at the lower class boundary for each ecological class under the WFD (*i.e.* high, good, moderate, poor)
Good ecological status	GES	The aspiration of the WFD (see below) that all surface waters reach this status by 2015
Load		Mass per time
Method 3		Load estimation algorithm from Littlewood.[1] Defined in Section 2.3
Method 5		Load estimation algorithm from Littlewood *et al.*[2] Defined in Section 2.3
Orthophosphate-P		Generic term used in the current study to describe P concentrations measured for regulatory purposes
Phosphorus limiting concentrations	PLC	River phosphorus concentration below which algal growth is nutrient limited
Population equivalent	pe	

(*Contd.*)

Term	Abbreviation	Definition
Q_{95} flow		Flow (in $m^3\ s^{-1}$) which was equalled or exceeded for 95% of the flow record
Reactive phosphorus	RP	Fraction of phosphorus passing through a 0.45 μm filter membrane and measured by the phosphomolybdenum blue colorimetric method
Sewage treatment works	STW	
Soluble reactive phosphorus	SRP	Fraction of phosphorus measured by the phosphomolybdenum blue colorimetric method after settling of suspended particles from the river water sample
Water framework directive	WFD	
Water information management system	WIMS	A chemical dataset collected and compiled by the Environment Agency of England

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