The role of alkalinity in setting water quality metrics: Phosphorus standards in United Kingdom rivers

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Abstract

UK implementation of the European Union Water Framework Directive (for the 2015 – 2021 cycle) Ecological Status (ES) classification for river phosphorus is based on the calculation of reference conditions for reactive phosphorus (RP) using river alkalinity measurements. Underpinning this approach is that the alkalinity is primarily from rock weathering and is free of anthropogenic influences. However, the potential contribution of anthropogenic alkalinity needs to be considered and, if possible, quantified. In the rural South West River Basin District of England, 38 river sites were examined with respect to river alkalinity loads in order to test this consideration. At river base flow when RP can cause enhanced algal growth, 9 sites (24 %) had effluent alkalinity contributions amounting to 25 – 49 % of the total riverine alkalinity load, while 11 (29 %) of the sites received ≥ 50 % of their alkalinity load from effluent.

When flows increased above base flow to Q_{95} flow at these 11 sites, catchment diffuse run-off became the largest load of alkalinity at 9 of the sites, and that at the Q_{95} flows, combined effluent and diffuse alkalinity loads contributed 68 – 100 % of the total alkalinity load. Anthropogenic alkalinity is likely to be present in diffuse run-off, but it is difficult to apportion alkalinity loads between natural and contaminant sources. It is likely that diffuse loads of alkalinity will dominate on the annual timescales used to assess WFD compliance, even at sites where ground water alkalinity dominates at base river flows.

In principle, inclusion of anthropogenic alkalinity in the calculation of ES boundary concentrations for RP may lead to a relaxation of the standards. In practice this may not follow. It is likely that at the river sites used initially to develop the algorithms now used for P standard setting, anthropogenic alkalinity was present, to

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varying and unknown degrees, and that this alkalinity would have influenced the measured and reference RP and biological metrics on which the P standards are based. Apart from RP, alkalinity is also used to underpin water quality metrics for additional chemical and biological parameters, and for this reason, understanding the complex factors determining river alkalinity loads should be an important task for water quality regulators.

1. Introduction

A key goal of the EU Water Framework Directive (WFD; 2000/60/EC) is to protect, enhance and restore all surface and ground waters with the aim of achieving Good Ecological Status (GES). With respect to eutrophication and riverine phosphorus, positive steps in reducing phosphorus concentrations in, principally urban, rivers, have been made due to improvements in sewage treatment. Nevertheless, there are still many rivers across the EU that are failing to achieve GES for this nutrient, including many in the UK.[1]

Revision of River Basin Management Plans for the second cycle of the WFD (2015-2021) has been undertaken, and in the UK new river phosphorus standards have been developed. Now, the key phosphorus component is defined as reactive phosphorus, or RP.[2-4] (RP is equivalent to the orthophosphate-P determinand reported for regulatory purposes by the Environment Agency (EA) of England, and is the molydate-reactive P measured on unfiltered samples from which large particles have been allowed to settle. RP is used instead of orthophosphate-P throughout the text.) Annual mean concentrations of RP are calculated which serve as standards in order to classify the Ecological Status of a river as High, Good, Moderate or Poor with respect to phytobenthos and macrophyte communities. The standards are in part based on the calculation of a reference RP concentration representing near natural conditions at a given site, expected in the absence of anthropogenic inputs, taking into account the alkalinity (as $CaCO_3$) of the river water at that site and the altitude of the site above sea level.[5,6] The concentration of alkalinity present is given to be a function of natural geological and geographic factors, including geochemical weathering of underlying rock at a particular site.[5,6] In more pristine rivers, largely unperturbed by anthropogenic inputs, this assumption is likely to be correct.

However, for rivers receiving sewage/industrial effluents and/or run-off from cultivated fields, this assumption is undermined, as these sources may contain substantial quantities of alkalinity (principally carbonate and bicarbonate, but also borate, organic acids and RP itself[7,8]). The alkalinity may enter the river from point sources or from diffuse runoff from a catchment that has received agricultural lime and/or wastewater from leaking septic tank systems and sewers.[9,10] Shallow ground waters, contaminated by wastewater, may also be a source.[11] In these rivers, inclusion of this anthropogenic alkalinity may, in principle, increase the concentration of RP defining each Ecological Status boundary, effectively providing a more 'relaxed' standard. The extent of this effect will depend on the loads of alkalinity from anthropogenic inputs relative to other sources; for the same anthropogenic alkalinity load the effect will be less for rivers fed from a limestone aquifer than for rivers fed by low alkalinity ground water or rivers of low base flow index (BFI). The effect may also be most pronounced in rivers that are subject to significant effluent flows during the lower river flow periods that typify the spring-summer in-river algal growing season in temperate zones.

The main aim of the current study was to determine if the anthropogenic component of the alkalinity load to rivers, from point and diffuse sources, is significant in the relatively low alkalinity rivers of the predominantly rural south west of England, a region in which more than 1000 water bodies are failing GES for RP.[12]

2. Methods

2.1. Study area

The South West River Basin District (SWRBD) has an area of ca. 21,000 km^2, and comprises ten main river systems, seven urban centres and numerous small settlements (Fig. 1). The human population is 5.3 million, although tourism is important and this figure increases markedly during the holiday periods.[12] By area, the region is 80 % rural, with land use dominated by agriculture (improved grassland for grazing, arable) and horticulture, and unimproved, acidic grasslands on the upland moors (Fig. 2a). The geology in the west of the region is composed of Carboniferous and Devonian age bedrock (sandstone, mudstones and shales), interspersed with granite intrusions (Fig. 2b). These rock formations contain little ground water, although shallow ground water is found in discrete alluvial deposits of sand and gravel in some river valleys. In the central part of the region (from the Somerset Levels south to the English Channel coast) the bedrock is overlain by sedimentary sandstone, mudstones and shelly limestone rock formations, and these are host to minor ground water aquifers. In the east is located a major chalk limestone aquifer, in part overlain by low permeability clays.[13]

2.2. Alkalinity load estimation

2.2.1. River base flow (Q_{river_min})

At river base flow, when ground water and effluent water dominate, the alkalinity loads from these sources can be estimated using equations 1 – 5:[14]

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

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

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

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

$$Q_{effluent} = \Sigma Q_{dwf\_effluent} \tag{5}$$

where L is alkalinity load in g s^{-1}, Q is flow in m^3 s^{-1}, dwf_effluent is treatment work dry weather flow and river_min is the minimum daily mean river flow for the period of interest. C is alkalinity concentration in g CaCO$_3$ m^{-3}. For each site, the sum of dwf_effluent discharge from each sewage (population equivalent > 250) and water treatment works contributing to flows at that site ($Q_{effluent}$) was calculated. Minimum (Q_{river_min}) river flows were derived from gauging station data for the periods for which river water alkalinity data were available (database window 1990 – 2014). The river flow data were from the UK National River Flow Archive, while effluent flow and alkalinity concentration data ($C_{effluent}$) were obtained from the Environment Agency of England Water Information Management System (WIMS) database. The dataset for alkalinity concentration was incomplete and not all works had data for the period of interest; in these cases, alkalinity data for the geographically nearest works were used. Concentrations of alkalinity in ground waters were from the British Geological Survey; these were reported as HCO$_3$$^-$ and were converted to the equivalent CaCO$_3$ concentration for the current study. Data for the hydrometric areas shown in Fig. 3 were reported in [11,15-17]. Location, flow and concentration data are collated in Table 1.

2.2.2. River flow greater than base flow

At river flows above base flow, diffuse run-off from the catchment, from the surface and unsaturated zone, will contribute to the river alkalinity load. It is important to estimate this load because, as discussed later, it will have both a natural and anthropogenic component. An estimate of the contribution of alkalinity from the catchment to a river site was derived from the value of the slope of the regression of alkalinity load vs flow, following[18]; this approach being particularly appropriate for the

predominantly low BFI river systems included in the current study. These authors used ordinary least squares regression (OLS) to quantify the relationship between load and flow, but in the current work the robust parametric bisquare weights linear regression was used because it is less sensitive to heteroscedastic data and the presence of outliers than OLS.[19,20] Concentration and flow data for all years for each site were used to estimate the slope value because the sampling frequency was generally only ca. 12 samples y^{-1} and alkalinity data were not available for all years. Bisquare weights regressions were undertaken using Matlab® R2016a.

The total alkalinity load, L_{river}, is the sum of:

$$L_{effluent} + L_{groundwater} + L_{diffuse} \tag{6}$$

where $L_{diffuse}$ is the catchment-integrated alkalinity load at a given river flow (g $CaCO_3$ s^{-1}). This resulting source apportionment model (SAM) is analogous to the Type 1 E-EMMA model described in[14], and assumes alkalinity is conservative at the temporal and spatial scales relevant to the current study. With this pragmatic SAM, the diffuse loads increase with river flow (thus for each 1 m^3 s^{-1} increase in flow the diffuse load (in g s^{-1}) increases by the value of the regression slope) while the effluent and ground water loads are assumed to remain constant throughout the year. It is assumed effluent loads are generally constant, although they would be expected to increase during the summer tourist season. In contrast, ground water loads may increase during and following the higher rainfall winter period, although the rivers examined here have relatively low base flow indices (BFI) of generally < 0.5,[21] and so this effect may be mitigated.

2.3. Water Framework Directive standards for reactive phosphorus

Phosphorus status is assessed by comparing measured RP concentration with standards based on site specific reference phosphorus concentrations. The RP

standard is the mean annual concentration estimated for the lower class boundary of the High, Good, Moderate or Poor Ecological Status (equation 7):

RP standard (μg P L^{-1}) = 10^((1.0497 $\log_{10}$(EQR) + 1.066) * ($\log_{10}$(reference RP) – $\log_{10}$(3500)) + $\log_{10}$(3500)) (7)

The Ecological Status depends on the value of EQR (Ecological Quality Ratio) used, where EQR is the site independent ecological quality ratio at the class boundary.[5,6] Equation 7 was derived from a regression relationship between biological EQR values (i.e. observed metric value / reference metric values) and a similar EQR for P (i.e. observed RP concentration / reference RP concentration). The biological EQRs were compared across Europe through a programme of intercalibration and the class boundaries used to determine the most likely EQR for P were derived using a re-arrangement of equation 7. The reference condition RP is the site specific RP concentration expected at near natural conditions, subject to local geology and hydrology. It is estimated from equation 8:

Reference RP = 10^(0.454($\log_{10}$alkalinity) – 0.0018(altitude) + 0.476) (8)

where alkalinity is the mean annual (or longer) total alkalinity (g CaCO$_3$ m^{-3}) of the water at a given site and the altitude is height (m) above sea level. The algorithm and parameter values were derived from 116 sites across the UK which either met intercalibration criteria for reference sites or which were thought to be only minimally impacted as indicated by environmental predictors.

3. Results and Discussion

3.1. Alkalinity load apportionment

3.1.1 River base flow (Q_{river_min})

The SAM was used initially to estimate alkalinity loads from groundwater and effluent at river base flow ($L_{baseflow}$) in order to estimate the importance of effluent alkalinity at ecologically sensitive times. The results from the 38 gauged river flow sites are presented in Fig. 4. Ground water alkalinity loads dominated at sites fed by the major chalk limestone aquifers in the east of the region, including the rivers Piddle, Frome and Hampshire Avon and its tributaries (gauging stations 44002, 44001, 43006, 43005 and 43021). The Parrett, and its tributaries the Tone and Isle (GS 52007, 52005 and 52004), were also in this category, probably because of the shelly limestone rock formations found locally giving rise to high alkalinity groundwater (Fig. 2b). Six of the 10 sites situated in hydrometric area 47 were also estimated to be dominated by ground water alkalinity, including the Tamar at Gunnislake (GS 47001), the Lyd and Inny tributaries of the Tamar (GS 47006 and 47020), the Walkham and Lumburn tributaries of the Tavy (GS 47014 and 47016) and the Plym (GS 47011). In terms of the contribution of point source loads of effluent to total alkalinity loads, 18 of the 38 sites showed effluent contributions of ≤ 24 %, while 9 of the 38 sites received effluent contributions of 25 – 49 %. At 11 sites, greater than 50 % of the total alkalinity at Q_{river_min} was estimated to be from effluent (Table 2). These sites were the Teign (50 % effluent alkalinity; GS 46002), the Exe at Thorverton (51 %; GS 45001), the Yealm (51 %; GS 47007), the Camel (53 %; GS 49001), the Tamar at Polson Bridge (57 %; GS 47019), the Torridge at Torrington (61 %; GS 50002), the Fal (63 %; GS 48003), the Erme (68 %, GS 46006), the Creedy tributary of the Exe (88%; GS 45012), the Taw (96 %, GS 50007 and the

Yeo tributary of the Parrett (100 %; GS 52006). The effluent load of alkalinity to the Taw at Taw Bridge (GS 50007) was estimated to comprise ca. 1 % from sewage treatment works (STW) and 95 % from the Taw Valley creamery. While there were effluent flow data for the creamery, alkalinity concentration data were lacking for this source. However, alkalinity concentration data for 2012-2013 were available for the nearby Davidstow creamery in north Cornwall, and the mean value of 898 g $CaCO_3$ m^{-3} (standard deviation was 267 g $CaCO_3$ m^{-3}) was adopted for the Taw Valley creamery. The effluent alkalinity concentration and flow data for the creamery and STWs located on the upper R. Taw (North Tawton, Belstone/South Tawton) were incorporated into a conservative dilution model for the short stretch of river reach between Belstone/South Tawton and Taw Bridge (distance ca. 12 km). The results from this model indicated that the creamery effluent was indeed likely to have been a significant contributor to the alkalinity concentrations measured at relatively low flows (i.e. < Q_{75}) at Taw Bridge, as shown in Fig 5. The result for the Yeo implies there was no groundwater contribution (i.e. effluent flow = river flow), although the river drains a region underlain by a minor limestone aquifer, as noted above. This may reflect difficulties in the accurate measurement of low river flows,[21] or poor constraints on effluent flow data, or both. This aspect of the veracity of the data is discussed later.

3.1.2 River flows greater than base flow

For the 11 sites with ≥ 50 % effluent contribution the SAM was used to extend the estimates of the relative importance of the ground water and effluent to include the catchment diffuse contribution to alkalinity loads as river flows increased. The SAM model with an example calculation is given in ESI 1. The catchment integrated diffuse concentrations were calculated for the 11 sites based on the WIMS locations

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and data periods given in Table 3. The results of the bisquare weights linear regressions are reported in Table 4. The positive linear relationships between alkalinity load and river flow gave significant ($p < 0.05$) R^2 values of ≥ 0.95 and mean slope values between 22.0 and 52.8 g $CaCO_3$ m^{-3}, except for the Yeo tributary of the Parrett (217 g $CaCO_3$ m^{-3}).

The three end-member SAM was used to apportion alkalinity loads for the Q_{95} flow for each of the 11 sites as this is a significant low flow parameter and particularly relevant in the assessment of river water quality consent conditions.[21] The results are given in Table 2 and Fig. 6 Relative to the base flow load apportionment, effluent alkalinity was less important at Q_{95} flows, and contributed less than half the load in all rivers except the Taw (92%) and the Yeo (51%). Thus, at the low Q_{95} flows, catchment run-off became the largest load of alkalinity at 9 of the 11 sites. The combined effluent and diffuse alkalinity loads for the 11 sites at Q_{95} flows contributed 68 – 100 % of the total alkalinity load in these low BFI, non-limestone, rivers. Diffuse loads at Q_{95} flows also became more important at sites where ground water alkalinity loads dominated at base flows. For example, at site GS 48011 on the Fowey, ground water contributed ca. 99 % of the total alkalinity load at the Q_{river_min} flow of 0.55 m^3 s^{-1}, while at the Q_{95} flow of 1.07 m^3 s^{-1}, the ground water contribution had decreased to 44 % and the catchment diffuse load increased to 55 %.

At higher Q_{75} flows, which still capture the generally lower flow conditions, diffuse run-off became even more dominant, accounting for 70 – 93 % of total alkalinity loads, except for the Fal (61 %) and Taw (36 %); the latter presumably because of the large inputs of alkalinity from the creamery (Fig. 6). By extrapolation, it would appear that on an annual basis, total alkalinity loads at all sites examined in

the current study, irrespective of the importance of groundwater or effluent at low flows, will be dominated by catchment run-off. This feature was perhaps unexpected at the outset of the study, and is a key finding. It is noteworthy that the concentrations of alkalinity in the catchment run-off were markedly higher than those measured in ground waters, except in the case of the Yeo (Table 5), suggesting that our approach in treating the two sources as distinct entities was reasonable.

As noted earlier, the overall diffuse load may have both natural and anthropogenic components. Clearly, natural weathering / leaching of carbonates from soils will provide a source of alkalinity, but this will vary as a function of, inter alia, soil composition in the unsaturated zone. Anthropogenic sources will include release of effluent from septic tank systems (STS), which are prevalent in rural areas,[9] and the application of limestone for pH control of agricultural soils (e.g.[10]). There are very few data on alkalinity loads from STS; reported alkalinity concentrations in STS effluents in the range 120 - 570 g $CaCO_3$ m^{-3} (mean ± sd, 330 ± 110 g $CaCO_3$ m^{-3}),[9] much higher than the run-off concentrations given in Tables 4 and 5. If per capita wastewater is 0.2 m^3 d^{-1}, then for a population of 1000 inhabitants (for example) in a given catchment, the alkalinity load would be 0.76 g $CaCO_3$ m^{-3} i.e. quite small relative to other anthropogenic sources. While evidence for alkalinity was not presented directly, there was some evidence of ground water contamination from domestic sources, including leaking sewers and septic tanks, in hydrometric areas 44, 45 and 52, with more limited evidence in the shallow ground waters in the west of the region.[11,15] Presumably, ground water contamination followed contamination of the adjacent unsaturated zones. While ca. 50 % of the agricultural soils in SW England are acidic, with pH values below the target range of 6 – 6.4,[22] regional application rates of limestone are difficult to find, and the British Survey of

Fertiliser Practice published annually by DEFRA report only summary data for liming. Thus, calculations suggest ca. 400,000 t limestone may be applied to soils in the SWRBD annually, but it is not possible to convert this to loads (as g $CaCO_3$ m^{-3}). In conclusion, the source apportionment of alkalinity within catchment run-off using this relatively simple approach remains to be resolved.

3.2 Environmental significance

In principle it is possible to calculate the GES concentrations RP at the sites examined in the current study using alkalinity with and without the estimated anthropogenic component. This was done for the 11 sites at which effluent alkalinity accounted for 50 % or more of the total alkalinity load at base flow (higher flow scenarios were not addressed because of the unknown anthropogenic component of catchment run-off alkalinity, as discussed earlier). The results are summarised in Fig. 7. Based on measured alkalinity data, only the Teign, Exe and Yealm consistently achieved GES with respect to RP. For the remaining sites, Ecological Status was lower, at Moderate or worse. Recalculation of the GES boundaries following subtraction of the estimated contribution of effluent alkalinity to the measured alkalinity results in decreases in the concentration boundaries of the GES window, with the effect that the occurrence of GES for RP is markedly reduced in the Teign and Yealm, and partly reduced in the Exe. For the remaining sites, achieving GES becomes more difficult. In practice, the application and usefulness of this approach may be blunted by an unaccounted component of anthropogenic alkalinity that was probably present in the river water at the sites used to draw up the observed and reference metric values for both RP and biology (diatoms, macrophytes) used to derive equations 7 and 8. Presumably the data exist which would allow the retrospective estimation of the relative importance of groundwater,

effluent and catchment alkalinity loads at the time of sampling, even if the net anthropogenic component cannot be calculated. This approach may then lead to revisions of equations 7 and 8, which may or may not be significant. It is also clear that given the apparent lack of pristine sites in the south west of England, and most probably in the wider UK, the methodology for calculating site specific standards is arguably quite limited unless estimates of alkalinity source apportionment, like those reported in the present work, are undertaken.

The results presented in the current work suggest that great care should be taken to ascertain (and quantify) the influence of discharges of anthropogenic alkalinity on site specific RP ES concentrations. The region examined was predominantly rural and anthropogenic pressures would be expected to be concominantly low. In more urban areas, human impacts would be greater, not only in the amount of waste water discharged, but in perhaps enhanced domestic contamination of ground waters and the urban equivalent of catchment diffuse run-off. Indeed, it is only recently that a pan-Great Britain study examining P (and N) impacts on rivers and headwaters in contrasting lowland/upland, high/low alkalinity systems was reported.[23] Measured RP concentrations were compared with calculated GES concentrations and conclusions drawn regarding management options for reducing RP concentrations. To what extent might the policy option suggestions be mitigated by the issues raised in the current work?

This study provides a first order assessment of the importance of alkalinity sources under contrasting river flows due to uncertainties in both the flow and concentration data used for load estimation. River flows can be difficult to measure accurately during low flow conditions because of catchment geology and land use, and because of abstractions and additions of water upstream of the gauging

station.[21] Despite this perceived uncertainty, in only one instance (the Yeo tributary of the Parrett), did the subtraction of the effluent dry weather effluent flow (a relatively well-constrained parameter) from Q_{river_min} result in a zero (indeed negative) ground water flow. In contrast to flows, concentrations of alkalinity in effluents were probably less-constrained because of absent or small datasets, and extrapolation of concentration data in a number of cases (perhaps most notably for the creamery at Taw Bridge). Additional uncertainties surround the parameterisation of alkalinity in ground water. For example, ground waters in hydrometric areas 44, 45 and 52 (Dorset and south Somerset) showed large variations in water chemistry,[15] and only in one region (Wessex Basin, hydrometric area 43) was a time series for carbonate available.[16] Finally, the estimation of the diffuse load of alkalinity for each catchment was based on an aggregate of many years of data, and it is not known if these aggregated values reflect actual temporal variability in alkalinity loads due, for example, to annual differences in run-off. Understanding temporal variability is likely to be key, given the apparent longer-term importance of this source, to setting appropriate boundary concentrations of RP.

The analysis reported herein is also likely to be of value in the wider context of UK ecological status assessment under the WFD because alkalinity is a key component of many chemical and biological assessment systems, often being used to split waters into "types" to facilitate the development of type specific reference metrics, e.g.[24] The third WFD river basin planning cycle is currently underway, providing an ideal opportunity to re-examine the role of alkalinity in status assessments at the national scale.

4 Conclusions

Calculation of WFD standards for river phosphorus in the UK is based on the calculation of site specific reference phosphorus concentrations using river alkalinity. In principle, the site specific approach appears highly desirable from a management perspective, but in practice the usefulness of the method may be limited by the general lack of riverine sites which exhibit natural or near-natural conditions, a pre-requisite for the approach. In the current work it has been demonstrated that, even in a region that is 80% rural by area, effluent alkalinity loads were ≥ 50% of total river alkalinity loads at base flows at a third of the sites examined. Inclusion of the effluent loads may, in principle, lead to relaxed RP boundary concentrations for GES. At higher Q_{95} and Q_{75} flows effluent loads diminished in importance but catchment diffuse loads of alkalinity increased markedly and on annual timescales are likely to dominate alkalinity loads to rivers, particularly the lower alkalinity, lower BFI rivers studied herein. Diffuse run-off is expected to be a conduit for anthropogenic alkalinity to rivers, but at this time it is not possible to quantify the anthropogenic component. However, it is conceivable that natural groundwater sourced alkalinity is a minor component of the total riverine load at many sites over longer timescales, thus exacerbating problems setting reliable RP GES concentrations.

Whether this finding is significant in respect of defining reliable reference RP concentrations and in turn reliable standard RP boundary concentrations is not straightforward however. This is because the measured and reference chemical and biological metrics at the original sites used to define the standard setting methodology may themselves have been influenced by unrecognised sources of anthropogenic alkalinity, although the extent of this influence is unknown. In the

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wider context of using alkalinity as a predictor of a range of biological and chemical metrics for water quality standard setting in the UK, it is clearly important to understand in more detail the factors that influence observed concentrations of alkalinity in surface waters, and for water quality regulators this should be given some priority.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

References

1 A. Civan, F. Worrall, H. P. Jarvie, N. J. K. Howden, T. P. Burt. Forty-year trends in the flux and concentration of phosphorus in British rivers. Journal of Hydrology 2018, 558, 314-327

2 Department for the Environment Food and Rural Affairs. Water Framework Directive implementation in England and Wales: new and updated standards to protect the water environment. 2014.

3 Department of the Environment. Consultation on the draft Water Framework Directive (Priority Substances and Classification) (Amendment) Regulations (Northern Ireland). 2014.

4 Scottish Environment Protection Agency. Supporting Guidance (WAT-SG-53). Environmental Quality Standards and Standards for Discharges to Surface Waters. 2015.

5 UK Technical Advisory Group. A revised approach to setting Water Framework Directive phosphorus standards phosphorus standards. 2012.

6 UK Technical Advisory Group. Phosphorus Standards for Rivers. Updated Recommendations. 2013.

7 C. Neal, H. P. Jarvie, M. Neal, A.J. Love, L. Hill and H. Wickham. Water quality of treated sewage effluent in a rural area of the upper Thames Basin, southern England, and the impacts of such effluents on riverine phosphorus concentrations. Journal of Hydrology 2005, 304, 103-117.

8 C.W. Hunt, J. E. Salisbury, and D. Vandemark. Contribution of non-carbonate anions to total alkalinity and overestimation of pCO2 in New England and New Brunswick rivers. Biogeosciences 2011, 8, 3069–3076.

9 P.J.A. Withers, H.P. Jarvie and C. Stoate. Quantifying the impact of septic tank systems on eutrophication risk in rural headwaters. Environment International 2011, 37, 644-653.

10 British Survey of Fertiliser Practice. Fertiliser use on farm crops for crop year 2014. Department for the Environment Food and Rural Affairs. 2016.

11 P.L. Smedley and D. Allen. Baseline Report Series 16: the Granites of South-West England, British Geological Survey Commissioned Report No. CR/04/255. 2004.

12 Environment Agency. Water for life and livelihoods. Part 1: South West river basin district. River basin management plan. 2016.

13 British Geological Survey regional geology overviews. South West England, The Hampshire Basin and adjoining areas, and Bristol and Gloucester region.

http://www.bgs.ac.uk/research/ukgeology/regionalGeology/home.html. Accessed January 2018.

14 H.P. Jarvie, C. Neal, P.J.A Withers, D.B. Baker, R. P. Richards and A.N. Sharpley. Quantifying phosphorus retention and release in rivers and watersheds using extended end-member mixing analysis (E-EMMA). Journal of Environmental Quality 2011, 40, 492–504.

15 P. Shand, P.E.L. Ander, K.J. Griffiths, P. Doherty, P. and A.R.P. Lawrence. Baseline Report Series 11: The Bridport Sands of Dorset and Somerset. British Geological Survey Commissioned Report No. CR/04/166N. 2004.

16 I. Neumann, J. Cobbing, A. Tooth and P. Shand. Baseline Report Series 15: The Palaeogene of the Wessex Basin. British Geological Survey Commissioned Report No. CR/04/254N. 2004.

17 W.M. Edmunds, P. Doherty, K. Griffiths, P. Shand and D. Peach. Baseline Report Series 4. The Chalk of Dorset. British Geological Survey Commissioned Report CR/02/268N. 2002.

18 D.M. Cooper, W.A. House, L. May and B. Gannon. The phosphorus budget of the Thame catchment, Oxfordshire, UK: 1. Mass balance. Science of the Total Environment 2002, 282-283, 233-251.

19 J.N. Miller and J. C. Miller. Statistics and Chemometrics for Analytical Chemistry, sixth edition. Pearson Education Limited. 2010.

20 A.D. Tappin, S. Comber and P. Worsfold. Orthophosphate-P in the nutrient impacted River Taw (SW England) between 1990 and 2013. Environmental Science: Processes and Impacts 2016, 18, 690-705.

21 T.J. Marsh and J. E. Hannaford. UK Hydrometric Register. Hydrological data UK series, Centre for Ecology & Hydrology. 2008.

22 SWARM Hub. https://www.swarmhub.co.uk/. Accessed January 2017.

23 H.P. Jarvie, D.R. Smith, L.R. Norton, F.K. Edwards, M.J. Bowes, S.M. King, P. Scarlett, S. Davies, R.M. Dils and N. Bachiller-Jareno. Phosphorus and nitrogen limitation and impairment of headwater streams in Great Britain: A national perspective on eutrophication. Science of the Total Environment 2018, 621, 849-862.

24 Water Framework Directive (Standards and Classification) Directions (England and Wales) 2015.

Table 1. Location, flow and alkalinity concentration data for the 38 river sites

River	Tributary	GS[a]	NRFA GS #	Lat (°N)	Long (°W)	Q_{river_min}[b] (m³ s⁻¹)	ΣQ_{dwf_stw} (m³ s⁻¹)	$Q_{groundwater}$ (m³ s⁻¹)	$C_{effluent}$[c] (g m⁻³)	$C_{groundwater}$ (g m⁻³)	Altitude (m AOD)[d]
Avon (Hampshire)		Amesbury	43005	51.171	1.785	0.734	0.071	0.663	175	246	73
Avon (Hampshire)	Nadder	Wilton	43006	51.076	1.863	0.571	0.013	0.558	175	246	56
Avon (Hampshire)		Knapp Mill	43021	50.748	1.780	4.340	0.578	3.762	289	246	2
Frome		East Stoke Total	44001	50.681	2.190	1.974	0.162	1.812	175	220	10
Piddle		Baggs Mills	44002	50.688	2.125	0.530	0.009	0.521	175	220	2
Exe		Thorverton	45001	50.804	3.511	1.460	0.093	1.367	105	7	25.9
Exe	Culm	Wood Mill	45003	50.842	3.393	0.909	0.047	0.862	105	7	44
Otter		Dotton	45005	50.688	3.295	0.643	0.069	0.574	169	243	18
Exe	Creedy	Cowley	45012	50.759	3.561	0.178	0.058	0.120	105	7	14.2
Teign		Preston	46002	50.559	3.618	0.606	0.053	0.553	74	7	3.8
Dart		Austins Bridge	46003	50.479	3.762	1.341	0.044	1.297	74	7	22.4
Erme		Ermington	46006	50.363	3.912	0.161	0.027	0.134	74	7	7.9
Dart	West Dart	Dunnabridge	46007	50.551	3.917	0.605	0.007	0.598	74	7	293
Avon (Devon)		Loddiswell	46008	50.313	3.802	0.250	0.005	0.245	74	7	28
Tamar		Gunnislake	47001	50.531	4.222	1.804	0.053	1.751	47	7	45
Lynher		Pillaton Mill	47004	50.440	4.300	0.322	0.024	0.298	47	7	8.5
Tamar	Lyd	Lifton Park	47006	50.635	4.281	0.496	0.006	0.490	47	7	51
Yealm		Puslinch	47007	50.343	4.005	0.112	0.010	0.102	74	7	5.5
Plym		Carn Wood	47011	50.431	4.084	0.273	0.003	0.270	74	7	51
Tavy	Walkham	Horrabridge	47014	50.509	4.098	0.152	0.001	0.151	44	7	87
Tavy		Ludbrook	47015	50.493	4.150	0.748	0.047	0.701	44	7	10
Tavy	Lumburn	Lumburn Bridge	47016	50.537	4.176	0.032	0.001	0.031	44	7	76
Tamar		Polson Bridge	47019	50.640	4.331	0.213	0.035	0.178	47	7	48
Tamar	Inny	Bealsmill	47020	50.570	4.319	0.193	0.003	0.190	47	7	47
Fal		Tregony	48003	50.266	4.919	0.326	0.041	0.285	117	10	6.9
Fowey	Loverny	Craigeshill Wood	48009	50.465	4.560	0.193	0.002	0.191	53	11	100

Fowey		Restormel	48011	50.431	4.681	0.545	0.002	0.543	53	11	16
Camel		Denby	49001	50.479	4.796	0.724	0.063	0.661	117	10	4.6
Taw		Umberleigh	50001	50.995	3.986	0.760	0.067	0.693	41	7	14.1
Torridge		Torrington	50002	50.946	4.138	0.468	0.085	0.383	123	7	13.9
Taw	Mole	Woodleigh	50006	50.973	3.910	0.445	0.018	0.427	32	7	67
Taw		Taw Bridge	50007	50.845	3.888	0.141	0.031[e]	0.110	41/898[f]	7	84.5
Torridge		Rockhay Bridge	50010	50.842	4.123	0.107	0.006	0.101	41	7	61
Torridge	W Okement	Jacobstowe	50011	50.799	4.001	0.277	0.026	0.251	41	7	90
Parrett	Isle	Ashford Mill	52004	50.964	2.913	0.248	0.098	0.150	154	243	14.6
Parrett	Tone	Bishops Hull	52005	51.019	3.135	0.371	0.069	0.302	154	243	20
Parrett	Yeo	Pen Mill	52006	50.943	2.609	0.196	0.208	-0.012[g]	154	243	23.9
Parrett		Chiselborough	52007	50.927	2.770	0.125	0.053	0.072	154	243	20.7

a, gauging station; b, Q, flow; c, C,concentration of $CaCO_3$; d, AoD, above ordnance datum; e, sum of sewage treatment work effluent flow (0.008 $m^3 s^{-1}$) and creamery effluent flow (0.023 $m^3 s^{-1}$); f, sewage treatment work effluent = 41 g m^{-3}, creamery effluent = 898 g m^{-3}; g, implies no ground water flow at Q_{river_min}.

Table 2. Source Apportionment Model (SAM) estimated contributions of effluent and diffuse alkalinity loads to total alkalinity loads for the 11 sites at which Q_{river_min} effluent alkalinity was ≥ 50 % of the total load

River	Tributary	Effluent alkalinity (%, Q_{river_min})	Effluent alkalinity (%, Q_{95})	Diffuse alkalinity (%, Q_{95})	Effluent + diffuse alkalinity (%, Q_{95})
Teign		50	29	43	72
Exe		51	24	53	77
Yealm		51	9	81	90
Camel		53	34	34	68
Tamar		57	10	82	92
Torridge		61	26	57	83
Fal		63	42	33	75
Erme		68	22	68	90
Exe	Creedy	88	42	52	94
Taw		96	92	5	97
Parrett	Yeo	100	51	49	100

Table 3. Site location and WIMS[a] alkalinity data used in the regression calculations

River	Tributary	WIMS alkalinity sampling site[b]	Lat (°N)	Long (°W)	WIMS alkalinity data period
Teign		Preston (46002)	50.559	3.617	2000-2004, 2007-2008
Exe		Thorverton (45001)	50.804	3.511	2000-2004, 2007-2013
Yealm		Yealm Bridge (47007)	50.351	3.983	2000-2010, 2013-2014
Camel		Grogley (49001)	50.483	4.799	2000-2005, 2007-2014
Tamar		Polson Bridge (47019)	50.640	4.331	2000-2005, 2007-2014
Torridge		Beam Bridge (50002)	50.967	4.175	2000-2003, 2007-2014
Taw		Taw Bridge (50007)	50.845	3.888	2000-2003, 2007-2010, 2013-2014
Fal		Tregony (48003)	50.266	4.919	2000-2004, 2007-2014
Erme		Sequer's Bridge (46006)	50.351	3.924	2000-2003, 2007-2014
Exe	Creedy	Oakford Farm (45012)	50.760	3.560	2000-2010, 2013-2014
Parrett	Yeo	A30 road bridge (52006)	50.942	2.609	2000-2005, 2007-2012

[a] WIMS; Water Information Management System. A national centralised water quality database managed by the Environment Agency of England

[b] number in brackets is nearest NRFA gauging station (given in Table 1)

Table 4. Concentrations of alkalinity calculated from the slope values of the bisquare weights regressions

River	Tributary	R^2	Slope (g CaCO$_3$ m^{-3})	Slope, 95 % CI[a] (g CaCO$_3$ m^{-3})	n[b]
Teign		0.99	23.1	22.4 - 23.9	49
Exe		0.97	30.5	29.6 - 31.3	158
Yealm		0.98	40.6	39.3 - 41.9	92
Camel		0.98	22.0	21.6 - 22.4	162
Tamar		0.99	34.4	34.1 - 34.7	166
Torridge		0.99	27.0	26.7 - 27.4	120
Taw		0.95	24.2	23.0 - 25.4	85
Fal		0.97	23.8	23.2 - 24.3	146
Erme		0.97	43.5	42.7 - 44.2	136
Exe	Creedy	0.97	52.8	51.4 - 54.3	119
Parrett	Yeo	0.99	217	215 - 219	150

[a] CI, confidence interval; [b] n, number of data points

Table 5. Concentrations of alkalinity (g CaCO$_3$ m^{-3}) in ground water and diffuse run-off

River	Tributary	Ground water	Diffuse run-off
Teign		7	23
Exe		7	31
Yealm		7	41
Camel		10	22
Tamar		7	34
Torridge		7	27
Fal		10	24
Erme		7	44
Exe	Creedy	7	53
Taw		7	24
Parrett	Yeo	243	217
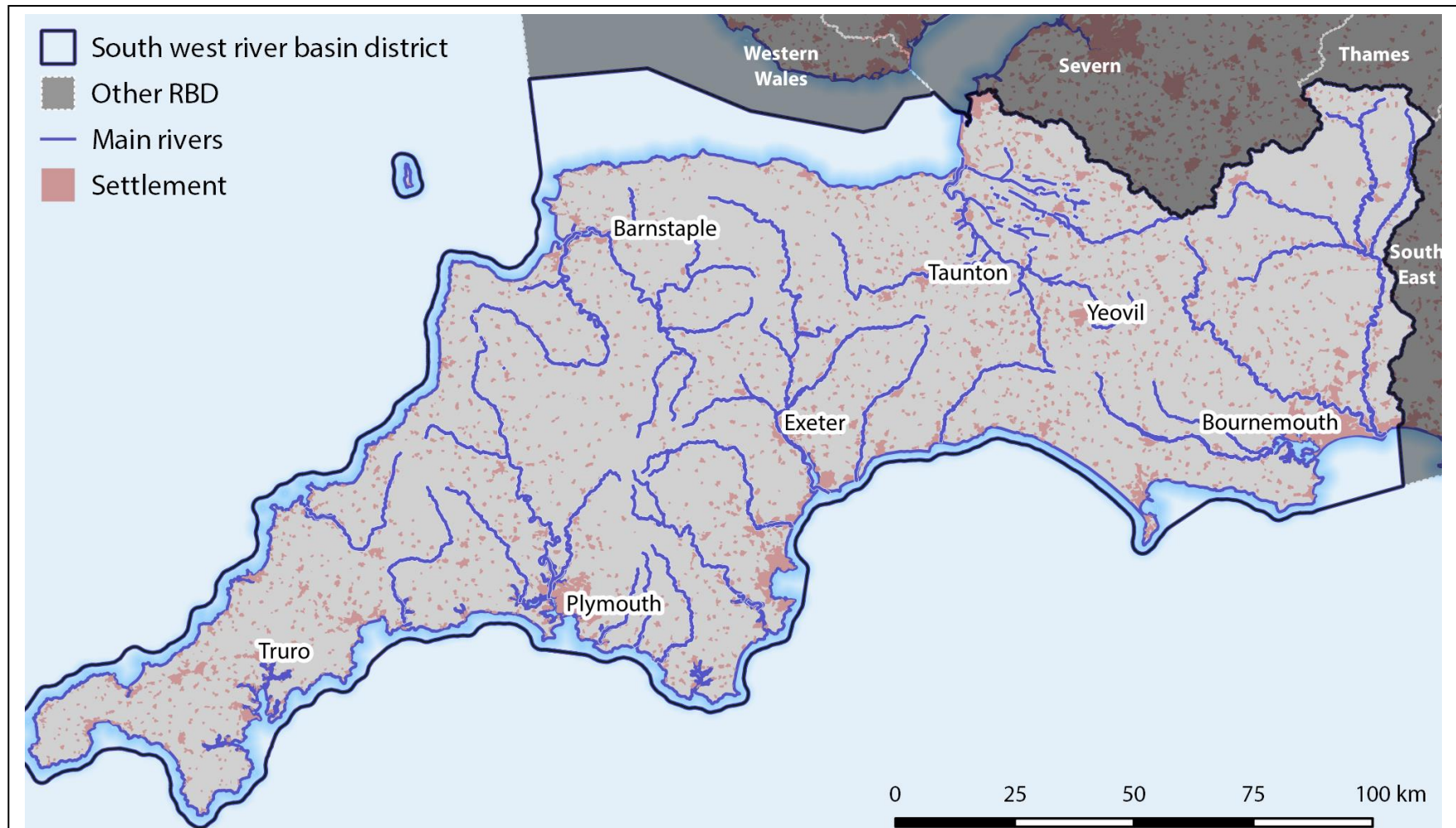
Figure 1. The South West River Basin District, main centres of population and main river network.

Figure 2(a) Main land use in the South West River Basin District

Figure 2(b) Main geology in the South West River Basin District (to 1 km depth)
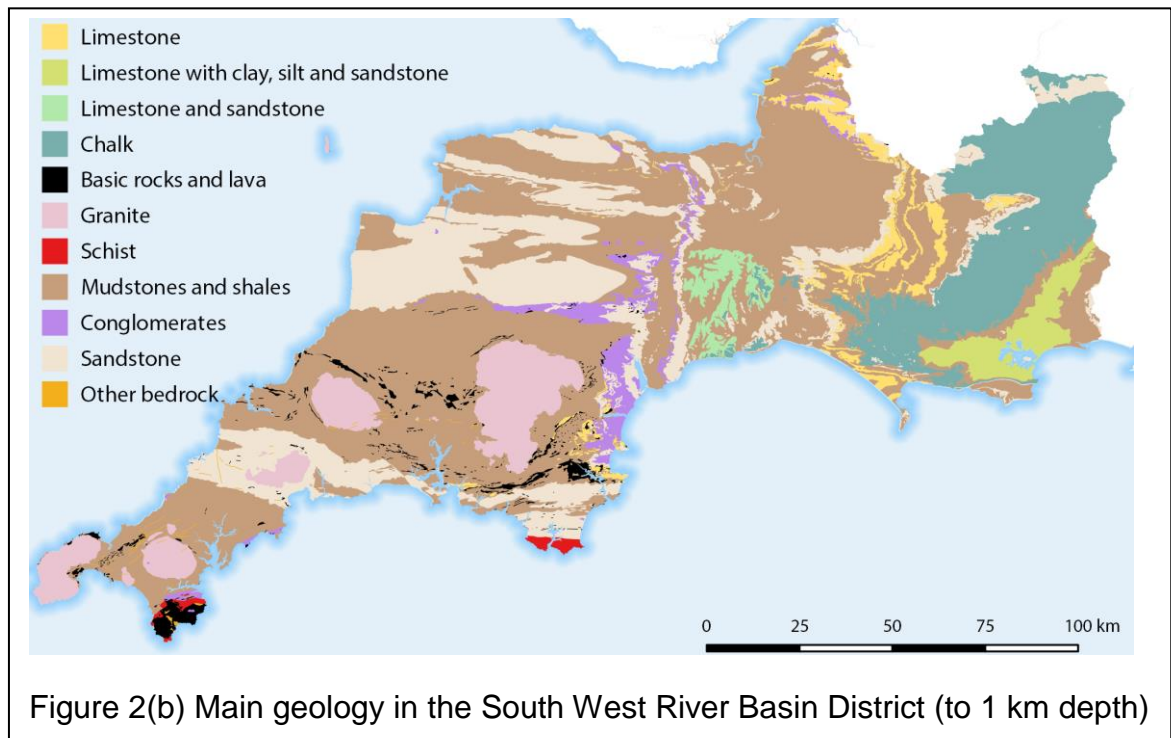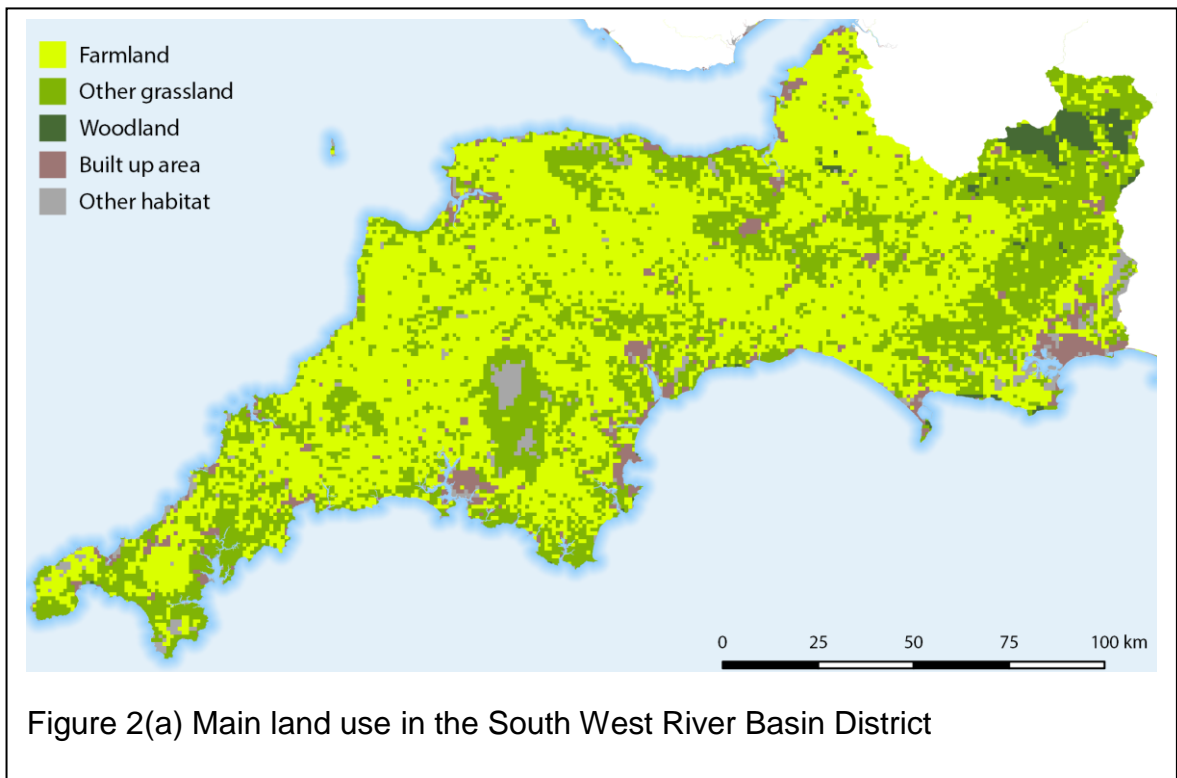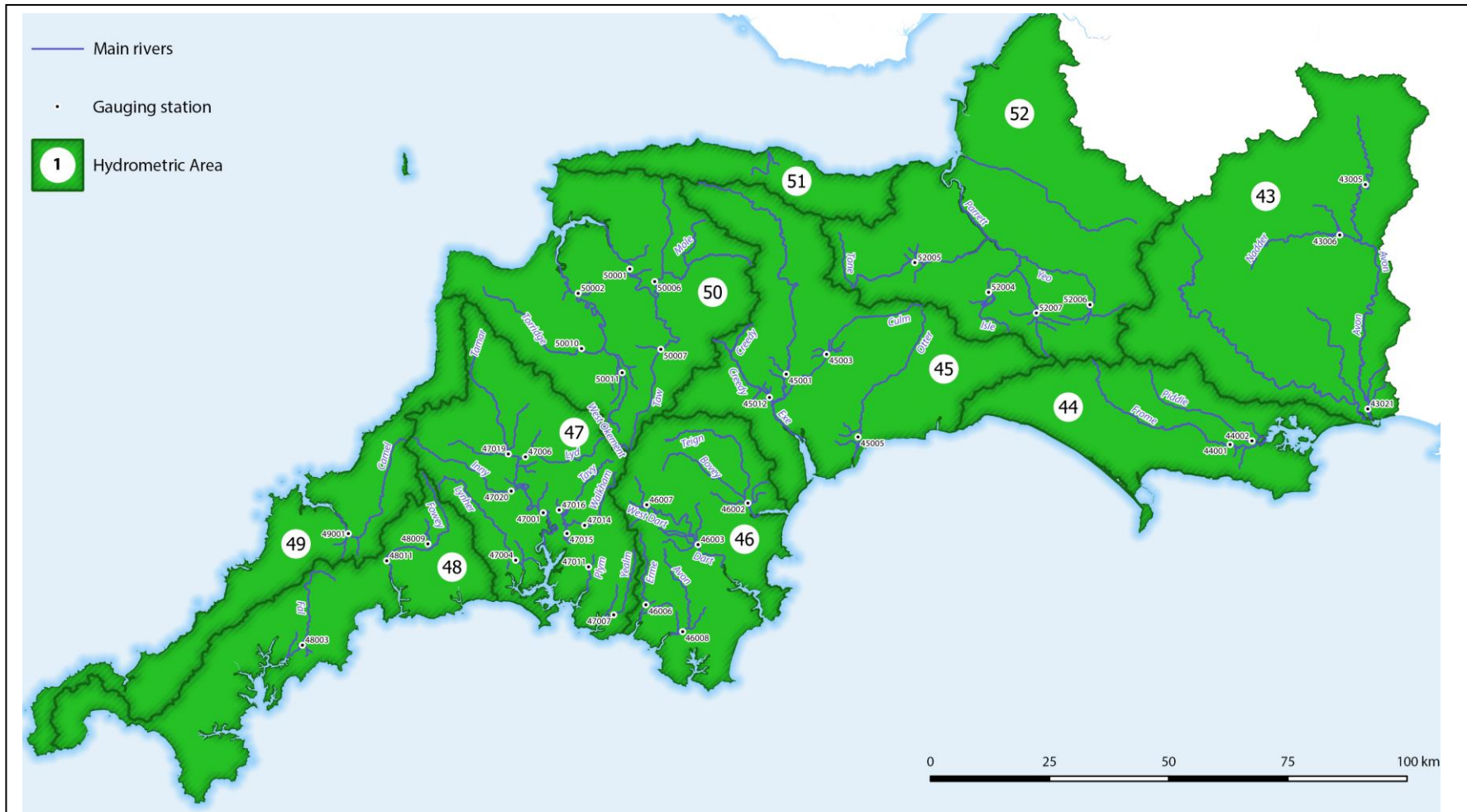
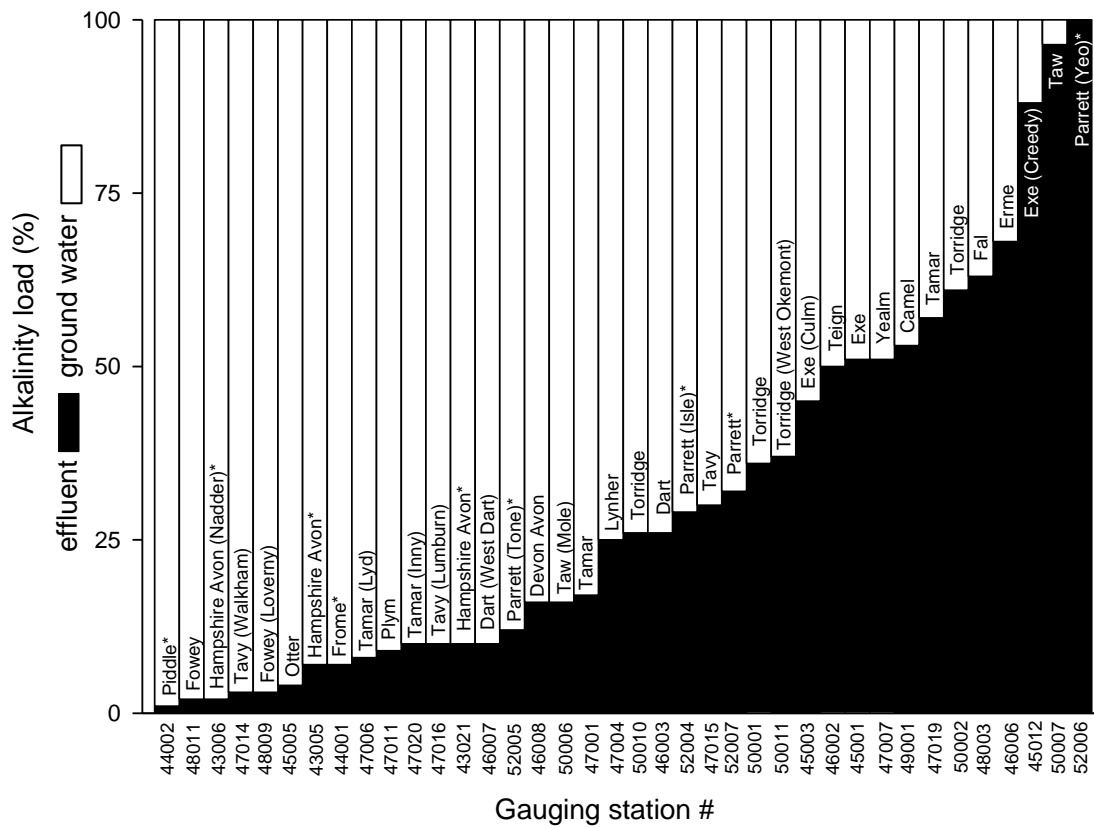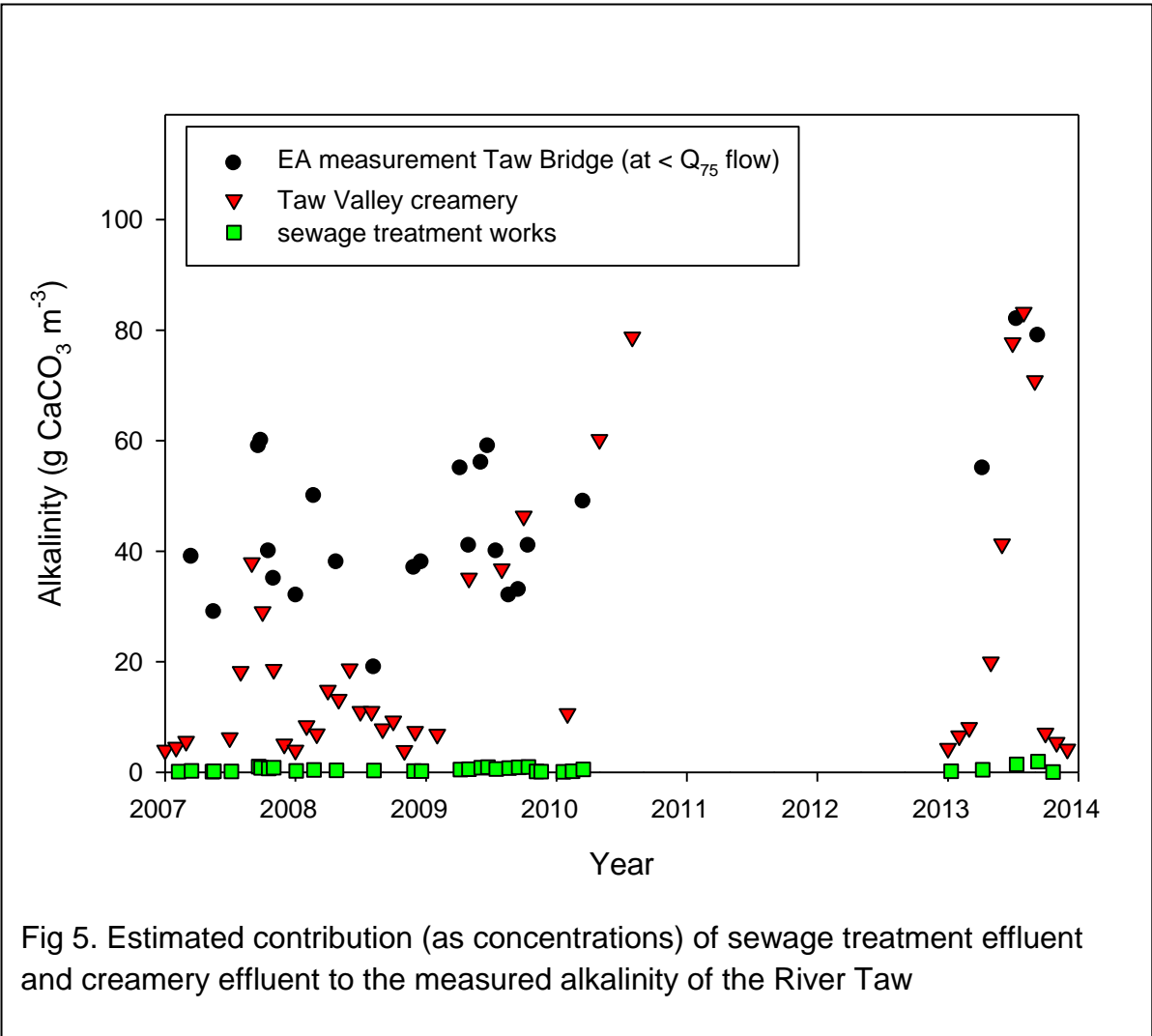Figure 3 Location of river gauging stations and extent of hydrometric areas.

Fig 4. Contributions (%) of ground water and effluent to total alkalinity loads at Q_{river_min}. Tributary names in brackets.
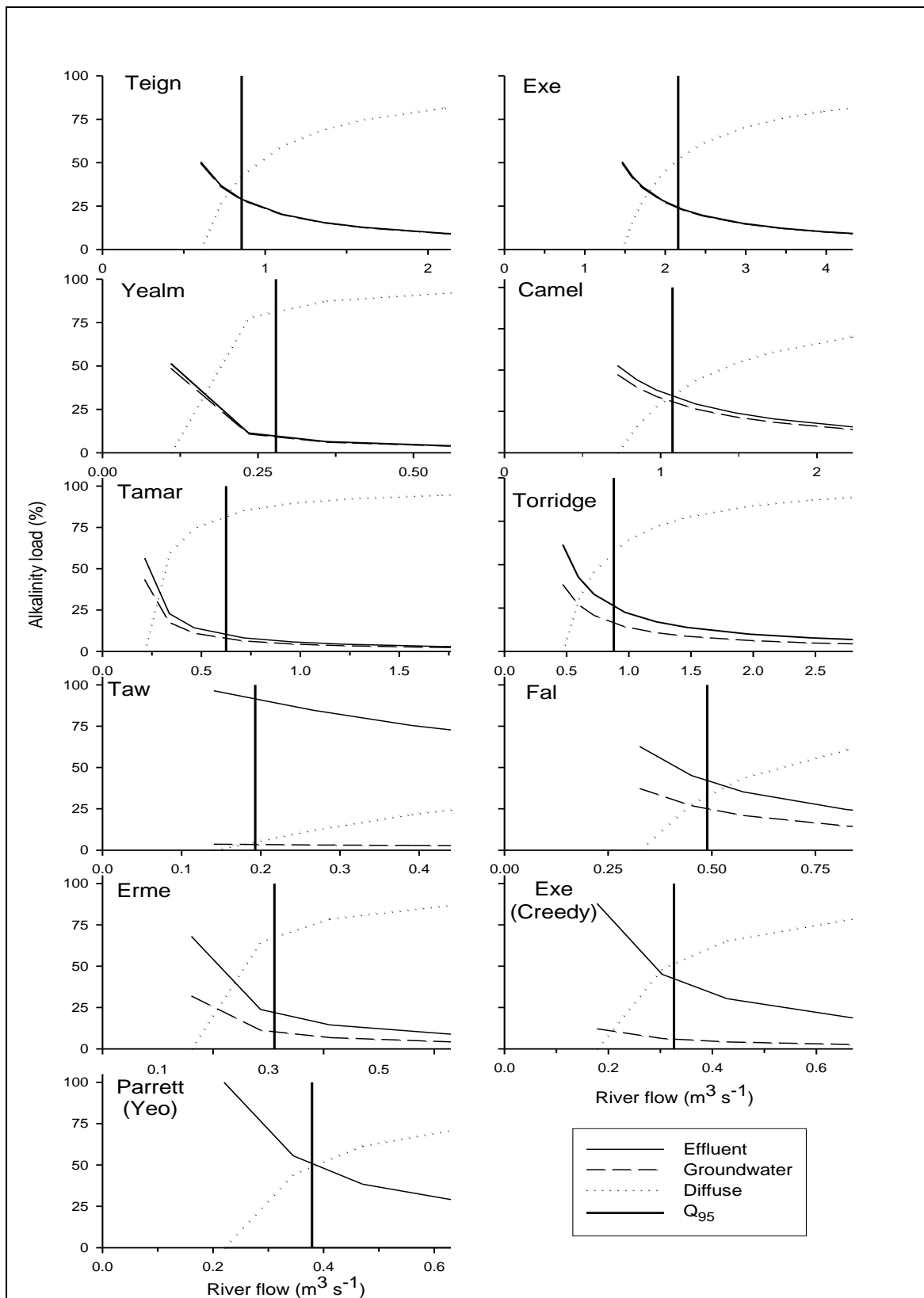
Fig 5. Estimated contribution (as concentrations) of sewage treatment effluent and creamery effluent to the measured alkalinity of the River Taw

Fig 6. Estimated contribution to total river alkalinity load from effluent, ground water and diffuse run-off as a function of river flow for the 11 sites with a ≥ 50% effluent contribution at base flow. X axis maximum is Q_{75} flow for each river. Q_{75} and Q_{95} flows are for the period of interest.
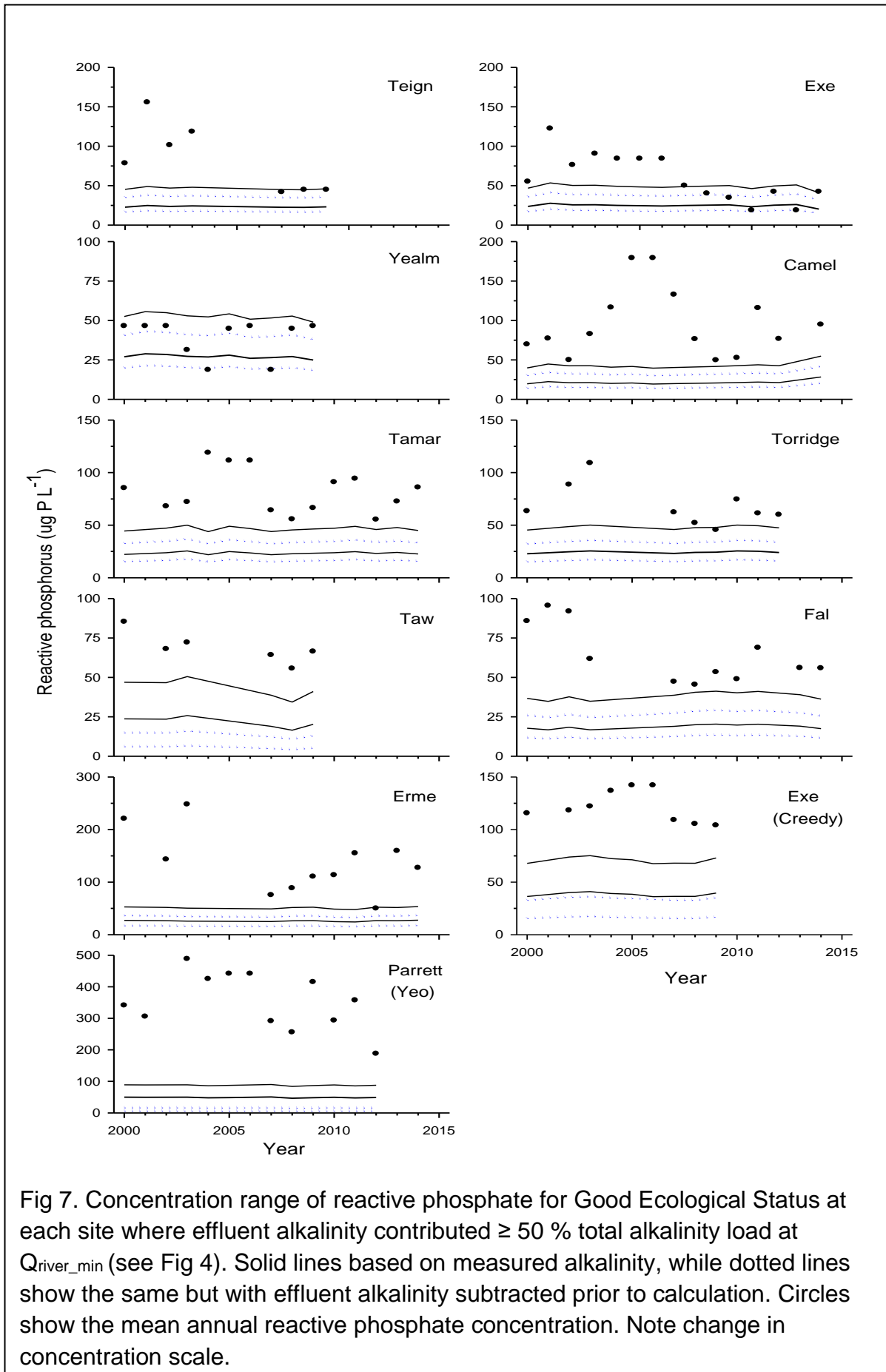
Fig 7. Concentration range of reactive phosphate for Good Ecological Status at each site where effluent alkalinity contributed ≥ 50 % total alkalinity load at Q_{river_min} (see Fig 4). Solid lines based on measured alkalinity, while dotted lines show the same but with effluent alkalinity subtracted prior to calculation. Circles show the mean annual reactive phosphate concentration. Note change in concentration scale.