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Evaluating the impacts of contrasting sewage treatment methods on nutrient dynamics across the River Wensum catchment, UK

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Abstract

Sewage effluent discharged from wastewater treatment plants (WWTPs) is a major driver of nitrogen (N) and phosphorus (P) enrichment, but tertiary treatment methods such as P-stripping have previously been shown to mitigate eutrophication risk. The aim of this study was to evaluate the impacts of sewage effluent discharged from WWTPs with contrasting classifications of tertiary treatment on nutrient dynamics across the River Wensum catchment, UK. River water samples were collected from 20 locations across the catchment at monthly intervals between October 2010 and September 2013, with 677 samples collected in total and analysed for a suite of hydrochemical parameters. The 20 sampling locations were divided into four classifications based on the type of upstream WWTP: (1) no WWTP; (2) WWTPs without P-stripping; (3) WWTPs with and without P-stripping; (4) WWTPs with P-stripping. Results revealed substantial overlaps in riverine nutrient composition making differentiation between classifications difficult. The majority of N (>97%) and P (~75%) was present in dissolved bioavailable forms across all sites and there was no significant difference in total N speciation between classifications. Total P (TP) speciation did, however, reveal higher proportions of particulate P at sites with no WWTP, indicating a greater P contribution of agricultural origin. Ratios of total dissolved to particulate P (TDP:TPP) and chloride concentrations proved effective discriminators of agricultural and sewage P, respectively, but phosphate-boron ratios (PO_4:B) were ineffective discriminators in this catchment. Most importantly, there was no evidence that P-stripping reduced overall TP concentrations downstream of WWTPs, despite evidence of a per capita reduction, nor

reduced the proportion of dissolved P released. These findings were attributed to P-stripping facilities serving larger populations and thus releasing greater effluent P load, thereby demonstrating that the presence of tertiary P-stripping alone is insufficient to overcome population pressures and ensure that rivers achieve good hydrochemical status.

Keywords: sewage; wastewater treatment works; water quality; nitrogen; phosphorus; river

1. Introduction

Sewage effluent discharged into rivers from wastewater treatment plants (WWTPs), also known as sewage treatment works (STWs) or water recycling centres (WRCs), represents one of the most important point sources of riverine nutrient pollution and is a major driver of freshwater eutrophication (Bowes et al., 2012a; Jarvie et al., 2006b; Neal et al., 2005). As naturally limiting nutrients of plant growth in aquatic systems, nitrogen (N) and phosphorus (P) enrichment fuels blooms of phytoplankton, periphyton and neuro-toxin secreting cyanobacteria colonies, which can dramatically lower species diversity and lead to a fundamental breakdown of ecosystem functioning (Hilton et al., 2006; O'Hare et al., 2018; Smith et al., 1999).

There are >9,000 WWTPs in the UK discharging an estimated 11 billion litres of wastewater into the environment daily (Yates et al., 2019). This sewage effluent is particularly rich in biologically available forms of N and P which are discharged at concentrations orders of magnitude greater than the concentrations required for river water to achieve '*good'* ecological and chemical status under the EU Water Framework Directive (2000/60/EC) (Demars et al., 2005; Edwards and Withers, 2008; Neal and Jarvie, 2005). Previous studies have, for example, observed increases in dissolved P concentrations of up to 2,000% downstream of WWTP outflows (Demars and Harper, 2005; House and Denison, 2002; Read et al., 2020), with particulate P also accumulating in, and being released from, downstream riverbed sediments (Jarvie et al., 2005; Palmer-Felgate et al., 2008; Roberts and Cooper, 2018). WWTP effluent is also rich in dissolved organic matter which acts as a carrier for heavy metal contaminants and promotes aerobic microbial decomposition in the receiving waterbody, increasing the biological oxygen demand (BOD) and thus leading to localised riverine hypoxia (Michael-Kordatou et al., 2015; Stanley et al., 2012).

Consequently, under the EU Urban Wastewater Directive (91/271/EC), WWTPs serving a population of 10,000–100,000 population equivalent (p.e.) have water quality restrictions for effluent discharging into a surface waterbody set at 2 mg P L^{-1} for total phosphorus (TP), 15 mg N L^{-1} for total nitrogen (TN) and 50 mg O_2 L^{-1} for BOD. These concentrations decrease to 1 mg P L^{-1} and 10 mg N L^{-1} for facilities serving >100,000 p.e. However, smaller facilities (<10,000 p.e.) have no legal requirement to meet such targets and concentrations in effluent discharges of up to 20 mg P L^{-1} and 100 mg N L^{-1} have previously been recorded, making small WWTPs a major catchment-wide eutrophication risk (Cooper et al., 2020a; Jarvie et al., 2006a; Neal et al., 2005; van Biervliet et al., 2020; Yates et al., 2019).

In order to reduce the environmental toxicity of sewage effluent, wastewater undergoes numerous stages of processing at WWTPs, including screening through filters to remove coarse material (pre-treatment), holding in settling tanks to encourage sedimentation of suspended fines (primary treatment) and promoting the degradation of organics through biological oxidation (secondary treatment) (DEFRA, 2002; Sonune and Ghate, 2004). However, post-treatment the effluent typically remains rich in nutrients and requires a further tertiary treatment to mitigate eutrophication risk. One such treatment is tertiary P-stripping, which involves dosing sewage effluent with an iron or aluminium salt (e.g. ferric chloride) which reacts with dissolved P to form a particulate P compound that is removed in settling tanks (Bunce et al., 2018; Clark et al., 1997). Whilst such tertiary treatment can be highly effective, removing up to 99% of P within WWTP effluent (Clark et al., 1997; Sengupta et al., 2015), the technology is expensive due to high capital and energy costs, and its application is generally limited to larger WWTPs serving population equivalents >10,000 and more sensitive waterbodies where the cost-benefit ratios are more favourable (Bunce et al., 2018).

The extent to which sewage effluent impacts upon nutrient cycling within river ecosystems, principally the balance between dissolved and particulate, organic and inorganic, and bioavailable and recalcitrant phases, is a key factor in determining the overall impact of WWTPs on water quality (Stutter et al., 2018; Trimmer et al., 2009; Withers and Jarvie, 2008) and such knowledge needs to be adequately captured within catchment management plans. In this context, the aim of this study was to investigate the impacts that contrasting classifications of wastewater treatment have on nutrient dynamics across the River Wensum catchment, UK – a river with multiple conservation designations suffering from nutrient enrichment and containing a substantial number of WWTPs. The main objectives were to:

i. Investigate the temporal dynamics of nutrient concentrations across 20 sites with and without upstream WWTPs between 2010 and 2013;

ii. Assess the impacts of contrasting methods of wastewater treatment on phosphorus and nitrogen speciation in the receiving waterbody;

iii. Identify unique sewage effluent nutrient signatures in wastewater discharged from different WWTP treatment classifications;

iv. Determine the major drivers of nutrient enrichment across the catchment;

v. Evaluate water quality in the context of the EU Water Framework Directive (WFD) standards to make an assessment on the overall health of the River Wensum.

The results of this study will provide valuable evidence on the extent to which effluent discharge from WWTPs is impacting upon water quality across the River Wensum catchment and the results can be viewed more broadly within a management context for similar sewage-impacted catchments in eastern England.

2. Methods

2.1 Study Location

The River Wensum, UK, is a 78 km length groundwater-dominated, lowland (source = 75 m AOD), calcareous river that drains an area of 660 km^2 and has a mean annual discharge of 4.1 m^3 s^{-1} near its outlet (52°40'06.35"N, 1°13'03.44"E; **Figure 1**). The catchment is underlain by Cretaceous White Chalk bedrock which is unconfined in the upper catchment and along sections of the river valley where the annual baseflow index (BFI) is 0.7–0.9. Over much of the rest of the catchment, the Chalk is confined by superficial deposits of Mid-Pleistocene diamicton glacial tills principally comprising chalky, flint-rich boulder clays of the Sheringham Cliffs (~0.2–10 m depth) and Lowestoft (~10–20 m depth) Formations **(Figure SM1)**. These are interspersed with layers of glaciofluvial and glaciolacustrine sands and gravels where the BFI is 0.5–0.7 (Cooper et al., 2018).

The main river channel is designated a Site of Special Scientific Interest (SSSI) and a European Special Area of Conservation (SAC) due to the diversity of its internationally important flora and invertebrate fauna and in recognition of it being one of the best examples of a lowland calcareous river in the world. However, 99.4% of the river habitat is in an unfavourable and declining state due to degraded morphology, sedimentation and eutrophication (Cooper et al., 2020b; Giakoumis and Voulvoulis, 2019). Arable agriculture (wheat, barley, sugar beet, oilseed rape) dominates land use (63%) with the remainder comprising 19% improved grassland, 9% mixed woodland, 5% unimproved grassland and 4% urban (Morton et al., 2011) **(Figure SM2)**. The mean annual temperature is 10.1°C and the mean annual rainfall total is 653 mm (1981-2010) (Meteorological Office, 2021).

There were 21 WWTPs across the catchment serving ~57,000 p.e., of which seven WWTPs had tertiary P-stripping technology installed (ferric chloride dosing) to reduce nutrient discharge at the time of this study. Metadata for the 21 WWTPs can be found in **Table SM1**. Previous modelling studies using SAGIS and SEPARATE estimated WWTPs were responsible for 26–47% of P in the River Wensum, compared with 29–40% derived from agriculture and 20–32% from other sources including urban runoff, storm tanks, atmospheric deposition and riverbank erosion (Natural England, 2015). In addition, there were ~1,863 properties off mains sewage served by domestic septic tank systems which were estimated to contribute a further 2–4% of the annual P load (Natural England, 2015).

2.2 Field Campaign

River water samples were collected from 17 tributary outlets and three main river sites across the catchment at approximately monthly intervals between October 2010 and September 2013, with 677 water samples collected in total during the field campaign (**Figure 1**). These 20 locations were divided into the following four categories:

1. Locations without an upstream WWTP (sites 2, 7, 9, 10, 16, 20, 21);
2. Locations downstream of WWTPs only without P-stripping (sites 1, 3, 4, 5, 17);
3. Locations downstream of WWTPs both with and without P-stripping (sites 6, 8, 13, 14, 15, 18);
4. Locations downstream of WWTPs only with P-stripping (sites 11, 12).

All sampling sites influenced by WWTPs were situated several kilometres downstream of the effluent outflow to ensure that the sewage discharge would be well mixed by the time it reached the sampling location. River water was grab sampled from the centre of the channel in 1 L acid pre-washed polypropylene bottles. All samples were transported in cool boxes and returned to cold storage (4°C) within 5 h to minimise biological degradation.

2.3 Laboratory Analysis

All water samples were analysed within five days of collection by the UEA Science Analytical Facilities (SAF) to determine concentrations of nutrients, carbon, major ions and total suspended solids (TSS). A Dionex ICS2000 Ion Chromatograph was used to determine concentrations of nitrate (NO_3), sulphate (SO_4) and Cl^-. A Skalar San++ Autoanalyser was used to determine concentrations of nitrite (NO_2), ammonium (NH_4), Si, total phosphorus (TP), total dissolved phosphorus (TDP), total reactive phosphorus (TRP) and phosphate (PO_4). Dissolved organic phosphorous (DOP) was calculated by subtraction of PO_4 from TDP concentrations, whilst total particulate phosphorus (TPP) was calculated by subtraction of TDP from TP. A Skalar Formacs CA15 TOC/TN analyser was used to determine concentrations of total nitrogen (TN), total dissolved nitrogen (TDN), total carbon (TC) and dissolved organic carbon (DOC). Total particulate nitrogen (TPN) was calculated by subtraction of TDN from TN concentrations, whilst dissolved organic nitrogen (DON) was calculated by subtraction of dissolved inorganic nitrogen (NO_3 + NO_2 + NH_4) from TDN. Lastly, an Agilent ICP-OES Vista Pro was used to determine concentrations of Al, B, Ca and Fe. Further details on instrument accuracy, precision and limits of detection can be found in **Table SM2**.

2.4 Data Analysis

To identify the hydrochemical signatures of sewage effluent, a principal components analysis (PCA) was undertaken on the standardized nutrient data (all N and P species) grouped by WWTP classification using the '*FactoMineR*' package in RStudio version 1.3.1093 (Le et al., 2008). An eigenvalue cut-off point of >1 was used as the criterion for retaining the principal components. Additionally, the non-parametric Kruskal–Wallis *H*-test was applied to identify which nutrient variables were significantly different between at least two WWTP classifications and thereby able to discriminate between them. A stepwise linear discriminant analysis (LDA) variable selection procedure based on the minimization of the Wilk's Lambda criterion was also employed to quantitatively determine the proportion of water samples that could be correctly classified to each WWTP classification based on nutrient concentrations alone.

Discharge data from the upper (site 13), mid (site 8) and lower (site 18) main channel of the River Wensum (**Figures SM4-6)** were obtained from the Centre for Ecology and Hydrology's National River Flow Achieve (CEH, 2020) (**Figure 2**) and used to calculate nutrient loads (discharge x concentration) and economic damage costs using the UK government (Defra) 2014 pollution prices (McGonigle et al., 2014). Water quality data were evaluated in the context of the EU Water Framework Directive (2000/60/EC), which had the original aim to ensure that all waterbodies within member states achieve '*good'* qualitative and quantitative status by 2015, although this has since been extended in most member states to the end of the second (2015–2021) and third (2021–2027) management cycles (Voulvoulis et al., 2017). For classification purposes, the Wensum tributaries sampled here were designated as small (10–100 km^2 catchment), lowland (mean altitude <200 m AOD), calcareous river systems with water quality standards for nitrate and total reactive phosphorus presented in **Table 1**.

3. Results and Discussion

3.1 Temporal Dynamics

Time series of monthly total phosphorus (TP) and total nitrogen (TN) concentrations recorded across the River Wensum catchment between October 2010 and September 2013 are shown classified by wastewater treatment type in **Figure 3**. The full hydrochemical dataset summarised by season is displayed in **Table 2**.

Over the full monitoring period, mean riverine TN concentrations were significantly (p < 0.05) highest at sites downstream of WWTP without P-stripping (9.07 mg N L^{-1}), followed by sites with and without P-stripping (8.33 mg N L^{-1}), sites with no WWTP (6.95 mg N L^{-1}) and WWTP sites with P-stripping (5.85 mg N L^{-1}). TN concentrations at sites without P-stripping were also found to display the most pronounced seasonal trends, with significantly (p < 0.05) higher mean concentrations observed during the winter (December – February; 11.0 mg N L^{-1}) compared to the summer (June – August; 7.2 mg N L^{-1}). Such seasonality is commonly associated with winter precipitation leaching soluble soil N into the shallow groundwater beneath agricultural land from where it discharges into the river network, either through the subsurface agricultural field drains or via upwelling through the riverbed, leading to elevated concentrations (Cooper et al., 2020b). During the spring (March – May) and summer, the reverse situation occurs as crops absorb soluble soil N and convert it into organic N leaving little residual soil N to be leached into groundwater (Burns et al., 2019; Outram et al., 2016). Considering that sites downstream of WWTPs without P-stripping had the highest percentage of catchment arable land cover at 74%, compared with 70% for sites with no WWTP, 60% for sites with and without P-stripping and 57% for sites with P-stripping, this indicates a predominantly diffuse agricultural pollution signal to the TN concentration data.

Conversely, TP concentrations displayed opposing seasonality to that of TN, with all sites downstream of WWTPs having ~46% higher mean concentrations during the summer/autumn than during the winter/spring **(Figure 3)**. This seasonal pattern can be explained by the continuous nature of sewage effluent discharge which results in: (a) a concentration of P-rich effluent during the summer and autumn period of lower river discharge; and (b) increased dilution during the winter and early spring period of higher river discharge (**Figure 2**; Bowes et al., 2012b; Withers and Jarvie, 2008). The environmental significance is a peaking of P concentrations during the most ecologically sensitive summer period when eutrophication risk is greatest. The exception to this were sites with no WWTP which had marginally higher TP concentrations during the winter (83 µg L^{-1}) than summer (73 µg L^{-1}), though not significantly (p = 0.154).

Over the full monitoring period, mean TP concentrations were significantly higher downstream of sites with P-stripping (227 µg L^{-1}), followed by sites with and without P-stripping (131 µg L^{-1}), without P-stripping (99 µg L^{-1}) and finally sites with no WWTP (75 µg L^{-1}). Thus, in contrast to previous studies (Jarvie et al., 2006a; Jarvie et al., 2002), there is no evidence that tertiary P-stripping has reduced the overall concentrations of P downstream of WWTPs.

3.2 Nutrient Speciation

The composition of TN and TP found across the River Wensum catchment can be seen in **Figure 4**. This reveals that TN was overwhelmingly dominated by dissolved inorganic NO_3, accounting for ~80% of TN throughout all seasons and across all classifications. The lack of seasonality in the proportion of NO_3 (range = 75–84%) was also apparent in the second largest component, DON, which accounted for 13–22% of TN. Marginally higher mean DON contributions were recorded at WWTP sites with P-stripping (20%) than at WWTP sites without P-stripping (16%), but overall there was little difference in the composition between the four classifications. The other two dissolved N fractions, NH_4 and NO_2, were both present at low concentrations (<2% contribution), indicating rapid nitrification of ammoniacal N in sewage effluent upon discharge into the river. Particulate N (TPN) was also only a minor component of TN, accounting for <3% across all sites and seasons, meaning that the vast majority (>97%) of TN existed in more readily bioavailable dissolved form, even at sites with no WWTPs. These results support very similar findings from other eastern UK rivers where NO_3 was found to account for up to 97% of TDN concentration and TPN accounted for ~5% of TN concentration (Jarvie et al., 1998).

In contrast to TN, TP speciation displayed greater seasonal variability and differences between WWTP classifications **(Figure 4)**. Dissolved inorganic PO_4 was the dominant component of TP across the catchment, but this varied substantially from a mean of 54% at sites with no WWTP to a mean of 70% at WWTP sites with and without P-stripping. Seasonally, PO_4 contributions also varied from generally higher proportions during the summer (61–81%) to lower proportions during the winter (50–66%), matching observations from other UK catchments (Bowes et al., 2003). The second largest component of TP was TPP, with the highest proportions of particulate P recorded at sites with no WWTP (mean = 36%), indicating a greater contribution at these sites is potentially derived from the erosion of P-rich arable soils in the absence of sewage effluent (Bowes et al., 2003). This is also supported by the proportion of TPP being generally higher during the winter when bare arable fields are exposed to higher erosion rates. The third largest component was DOP, which accounted for 2–16% of TP. This organic P fraction displayed no consistent seasonality across WWTP classifications, although the highest proportions were recorded during the spring and summer seasons at sites downstream of WWTPs.

Overall, across the whole catchment a lower proportion of TP (~75%) was in readily bioavailable dissolved form compared to TN (>97%), but the dynamic nature of P cycling is such that particulate forms remain a eutrophication risk (Withers and Jarvie, 2008). Again, these results support very similar findings from other eastern UK rivers where TDP and TPP accounted for 71–92% and 7–29% of TP, respectively (Jarvie et al., 1998). Importantly, however, there was also no evidence that tertiary P-stripping reduced the proportion of dissolved P downstream of WWTPs where it was installed.

3.3 Effluent Nutrient Signatures

The results of the PCA are displayed in **Figure 5** for the first four components with eigenvalues >1, which collectively explained 72.2% of the variance in the entire dataset of N and P species. PCA biplots reveal the degree of differentiation in hydrochemistry downstream of the four WWTP classifications, whilst variable correlation plots display the relationships between all nutrient parameters. Positively correlated variables are grouped together, whilst negatively correlated variables are positioned on opposite sides of the plot origin. The distance between the variables and the origin (i.e. the length of the arrow) represents the factor loadings, with longer arrows indicating the variable yields greater discrimination between the four WWTP classifications.

The PCA biplots for all four components revealed substantial overlaps in the river nutrient composition downstream of each WWTP classification, implying that differentiation between WWTP groupings based solely on N and P species concentrations is difficult. The notable exception was for WWTPs with P-stripping where four highly correlated P species (PO_4, TRP, TDP, TP) were found to be the strongest discriminators in PC1 (33.3% of total variance), reflecting the elevated concentrations of dissolved forms of P recorded at these sites **(Table 2)**. For PC2, explaining 18.6% of the total variance, overlaps were again substantial although three highly correlated N species (NO_3, DON, TN) provided some degree of differentiation between WWTPs with P-stripping and WWTPs with and without P-stripping, reflecting higher concentrations of these forms of N in the latter. For PC3, explaining 10.9% of the total variance, two N species (NH_4 and NO_2) and the TDP:TPP ratio provided the strongest discrimination for WWTPs with P-stripping, with higher N species concentrations and lower P ratios found at these sites.

Despite the strong degree of overlap in the nutrient compositions within each WWTP classification, the Kruskal-Wallis *H*-test revealed that all nutrient variables, with the exception of TPN, were significantly different ($p < 0.01$) between at least two classifications and thus were able to discriminate between at least two types of WWTP **(Table 3)**. Furthermore, linear discriminant analysis identified NO_3 as the strongest individual discriminator between classifications, in contrast to the PCA, capable of successfully differentiating 44.0% of water samples by WWTP classification. However, even combined with the other 12 nutrient variables, just 51.1% of water samples could be correctly differentiated by classification type using LDA, reflecting the substantial degree of overlap in the nutrient compositions of the river water across the catchment.

3.4 Drivers of Nutrient Enrichment

To determine the major point and diffuse source pollution drivers of nutrient enrichment across the catchment, several different metrics were explored including nutrient ratios and chloride concentrations **(Figure 6)**, and land use proportions and precipitation totals **(Figure 7)**.

The ratio of P to boron (B) in river water has previously been demonstrated to effectively discriminate between P derived from sewage effluent (lower P:B ratio) and P derived from agricultural fertilisers (higher P:B ratio) due to the enrichment of wastewater in boron containing laundry detergents (Jarvie et al., 2006b). Here, however, boron concentrations were relatively low across all sites (WWTP classification means = 29 – 33 μg L^{-1}) and were not significantly ($p > 0.05$) lower at sites with no WWTP **(Table 2)**, thus indicating that the PO_4:B ratio is not an effective discriminator of sewage and agricultural P pollution in this catchment. Consequently, differences in PO_4:B ratios between WWTP classifications were driven largely by differences in PO_4 concentrations, with significantly higher ratios recorded at WWTP sites with P-stripping (mean = 6.8) than all other sites (means = 2.1 – 4.9), matching the patterns shown in **Figure 4**.

Whilst P is readily cycled between different phases within aquatic environments (Withers and Jarvie, 2008), the ratio of dissolved to particulate fractions of P can provide an indication of the amount of P derived from allochthonous sources such as the erosion of P-rich agricultural soils which dominantly occurs in particulate form (Palmer-Felgate et al., 2009), verses P derived from WWTPs which dominantly occurs in dissolved form (Yates et al., 2019). Here, TDP:TPP ratios were indeed significantly lower at sites with no WWTP (mean = 2.8) than those with WWTPs (means = 3.9 – 7.8), with this higher proportion of particulate P indicating a stronger agricultural control on nutrient enrichment at the no WWTP sites **(Figure 6)**. Furthermore, significantly higher TDP:TPP ratios at all WWTP sites during the summer months (means = 6.9 – 15.3; **Table 2**) emphasise considerable dissolved P loading from WWTPs during periods of low river discharge, a trend not observed at sites with no WWTP.

Another useful proxy for determining the proportion of river water derived from sewage effluent are chloride concentrations. Chloride is typically enriched in sewage effluent due to chlorination during drinking water treatment and by comparing chloride at sites with and without WWTPs (i.e. impact and control) it is possible to estimate the percentage of total river flow at each site derived from wastewater. Mean chloride concentrations were 39.6 mg L^{-1} at no WWTP sites, 43.3 mg L^{-1} at sites with and without P-stripping, 46.7 mg L^{-1} at sites without P-stripping and 47.5 mg L^{-1} at sites with P-stripping **(Figure 6)**. Therefore, assuming a background chloride concentration of 39.6 mg L^{-1} and that all chloride enrichment was derived from sewage effluent, the mean proportion of total river flow derived from WWTPs was 9.3% at sites with and without P-stripping, 17.9% at sites without P-stripping and 19.9% at sites with P-stripping. These estimated proportions are largely supportive in explaining the temporal trends in TP observed in **Figure 3**.

The relationships between the percentage arable land cover upstream of the 20 sampling sites and the mean riverine nutrient concentrations are shown in **Figure 7**. This reveals a modest and significant ($p < 0.05$) positive correlation between TN and arable land cover (R^2 = 0.223), whereas the correlation between TP and arable land cover is weak (R^2 = 0.030) and insignificant (p = 0.466). These results further support that variability in P concentrations are largely driven by WWTP discharge, whereas variability in N concentrations largely have an agricultural origin.

The relationships between mean nutrient concentrations and precipitation totals in the 24 hours prior to sampling are also shown in **Figure 7**. This reveals that neither TN nor TP concentrations were significantly correlated with precipitation totals at this timescale, which likely reflects the inability to fully capture the dynamic hysteresis behaviour that characterises nutrient concentrations during precipitation events (Outram et al., 2016). The relationships with precipitation totals at 2-7 days prior to sampling were also tested but yielded even weaker correlations.

3.5 Effectiveness of P-stripping

Whilst the results presented in **Figures 3 & 4** revealed no evidence that tertiary P-stripping had reduced the 'overall' concentration of P downstream of WWTPs, there was evidence that effluent P concentrations were reduced on a per capita basis. WWTPs with P-stripping served a larger population (mean = 7,296 p.e.) compared to those without P-stripping (mean = 568 p.e.) **(Table SM1)**, meaning these P-stripping facilities discharged a higher effluent P load into the river (~12.8 times greater), thus explaining the higher mean TP concentrations observed at P-stripping sites (227 µg L^{-1}) compared to sites without P-stripping (99 µg L^{-1}). However, if one assumes all TP in the river was derived from sewage effluent, then the TP concentration downstream of WWTPs with P-stripping was 0.031 µg L^{-1} $p.e.^{-1}$ (227 µg L^{-1} / 7,296 p.e.) compared with 0.174 µg L^{-1} $p.e.^{-1}$ (99 µg L^{-1} / 568 p.e.) downstream of WWTP without P-stripping. This indicates an ~82% P-stripping removal efficiency which is comparable with previous studies (e.g. Bunce et al., 2018) and implies that it is population pressure, rather than P-stripping effectiveness, that is the dominant control on riverine P concentrations.

3.6 Water Framework Directive (WFD) Status

Applying the EU Water Framework Directive standards for NO_3-N and TRP **(Table 1)** to the four WWTP classifications revealed two main findings: (i) sites with no WWTP had the highest level of water quality and (ii) elevated nitrate concentrations were the primary reason for failing to achieve '*good'* hydrochemical status in the River Wensum **(Figure 8)**. The percentage of water samples achieving '*good'* or '*high'* status for nitrate ranged from 24% for sites with no WWTP to 9.6% for sites with P-stripping, 7.4% for sites without P-stripping and just 1.4% for sites with and without P-stripping. With respect to the EU Drinking Water Directive (98/83/EC) standard for nitrate (11.3 mg N L^{-1}), WWTP sites without P-stripping recorded the highest proportion of exceedances at 9.7%. For TRP, the percentage of water samples achieving '*good'* or '*high'* status ranged from 87.5% for sites with no WWTP to 65.2% for sites without P-stripping, 57.8% for sites with and without P-stripping and 39.7% for sites with P-stripping.

Therefore, despite the presence of tertiary treatment technologies, sites downstream of WWTPs with P-stripping had the poorest water quality with respect to P, whilst nitrate concentrations were the primary driver of poor hydrochemical status across the entire River Wensum catchment. This observation is supported by the TDN:TDP ratios **(Table 2)** which reveal that all sites are P limited, with mean mass ratios of 23–175 across the catchment being substantially greater than the Redfield mass ratio of 7.3 (Jarvie et al., 1998).

To quantify the economic impact of this nutrient enrichment, pollution damage costs were derived for site 18 by calculating TP, TN and TSS annual loads and multiplying by the 2014 UK pollutant prices **(Table 4)**. These generic pollutant prices, which relate to overall riverine pollution concentrations rather than pollution from a specific source, account for remediating the ecological impacts of the pollutants (e.g. tackling eutrophication), making water potable (e.g. tertiary water treatment costs to remove N) and the cost of keeping rivers navigable (e.g. dredging costs to remove excess sediment and aquatic vegetation). This analysis revealed 864 tonnes of N, 629 tonnes of sediment and 12 tonnes of P were exported out of the River Wensum catchment annually, contributing to a combined annual damage cost of £559,426.

4. Conclusions

The results of this study have demonstrated the impacts that contrasting classifications of wastewater treatment have on nutrient dynamics across the River Wensum catchment, UK, and the key research findings can be summarised as follows:

- **i.** River Wensum nutrient concentrations exhibited contrasting seasonality across all WWTP classifications, with N concentrations increasing during the winter and decreasing during the summer, indicative of agricultural pollution, whilst P concentrations increased during the summer and decreased during the winter, indicative of sewage effluent pollution;

- **ii.** The vast majority of riverine TN (>97%) and TP (~75%) were present in dissolved bioavailable form across all sites. There was no significant difference in TN composition between the four WWTP classifications, however, TP speciation revealed a higher proportion of particulate P (36%) at sites with no WWTP, indicating a greater P contribution derived from the erosion of P-rich agricultural soils;

- **iii.** Principal components analysis revealed substantial overlaps in riverine nutrient composition across all 20 sites making differentiation between WWTP classifications difficult. Only 51% of water samples could be correctly assigned to their WWTP classification based solely on N and P species concentrations;

- **iv.** There was no evidence that tertiary P-stripping reduced 'overall' TP concentrations downstream of WWTPs, despite evidence of a per capita reduction, nor reduced the proportion of dissolved P released. This is due to P-stripping facilities serving larger populations and thus releasing greater effluent P load than WWTPs without P-stripping. These findings therefore demonstrate that the presence of tertiary P-stripping alone is insufficient to overcome population pressures and ensure that rivers achieve good hydrochemical status;

v. TDP:TPP ratios and chloride concentrations proved effective discriminators of agricultural and sewage P pollution, respectively, but PO_4:B ratios were ineffective discriminators in this catchment;

vi. Elevated nitrate concentrations were the primary reason for the failure to achieve '*good'* hydrochemical status across the River Wensum catchment, with the highest level of water quality found at sites with no WWTPs.

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Dataset

The full dataset used in this study can be freely accessed under an Open Government Licence here: Cooper RJ, Hiscock KM. 2021. Water quality data from the River Wensum, UK, 2010-2016. NERC Environmental Information Data Centre. https://doi.org/10.5285/71ddb087-59e6-432a-8d3e-72cbce251ee9

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Figure Captions

Figure 1: River Wensum catchment, UK, showing the locations of wastewater treatment plants (WWTPs) and river water sampling sites.

Figure 2: Annual hydrographs for the River Wensum recorded at gauging stations located in the upper (site 13), middle (site 8) and lower (site 18) catchment during the period 1960–2019 (CEH, 2020). See locations on Figure 1. Dotted line represents the mean discharge during the October 2010–September 2013 study period. Red and blue shading represents the lowest and highest flows on each day over the period of record.

Figure 3: Time series of total phosphorus (TP) and total nitrogen (TN) concentrations recorded across the River Wensum catchment between October 2010 and September 2013.

Data presented as the mean concentration for each WWTP classification with ± 1 standard error shading.

Figure 4: Mean seasonal phosphorous **(top)** and nitrogen **(bottom)** speciation across the River Wensum catchment differentiated by WWTP classification. Numbers on the bars represent the percentage contribution of each fraction to the total concentration.

Figure 5: Principal component analysis plots of River Wensum hydrochemistry for the first four principal components. **(Left)** biplots with data grouped by WWTP classification; shaded ellipsoids encompass 50% of the group range. **(Right)** variable correlation plots with arrow length proportional to the factor loading.

Figure 6: Boxplots of nutrient ratios and chloride concentrations measured at sites across the River Wensum catchment differentiated by WWTP classification. 1 = No WWTP; 2 = WWTP no P-stripping; 3 = WWTP with and without P-stripping; 4 = WWTP with P-stripping. Numbers inside boxplots represent the number of samples.

Figure 7: **(Left)** correlation of mean TN and TP concentrations against percentage upstream arable land cover for all 20 sampling sites; **(Right)** correlation of TN and TP concentrations against precipitation totals recorded in the 24 hours prior to sample collection.

Figure 8: EU Water Framework Directive (WFD) status classifications for the River Wensum for the period October 2010 – September 2013.

Table 1: EU Water Framework Directive (WFD) thresholds applied to the River Wensum to assess water quality status (UKTAG, 2013).

Parameter	**EU WFD Physico-chemical Status**				
	Bad	**Poor**	**Moderate**	**Good**	**High**
Nitrate (mg N/L)	>11.3	>5.6 – 11.3	>3.6 – 5.6	>0.8 – 3.6	< 0.8
TRP (mg P/L)	>1.003	>0.173 – 1.003	>0.069 – 0.173	>0.036 – 0.069	<0.036

Table 2: Mean seasonal hydrochemical concentrations for the River Wensum recorded between October 2010 and September 2013 across 20 sites grouped by four different wastewater treatment plant classifications. TSS is total suspended solids.

	Parameter	No WWTP				WWTP No P-stripping				WWTP With and without P-stripping				WWTP With P-stripping			
		Spr	*Sum*	*Aut*	*Win*	*Spr*	*Sum*	*Aut*	*Win*	*Spr*	*Sum*	*Aut*	*Win*	*Spr*	*Sum*	*Aut*	*Win*
Nitrogen Species	NO_3 (mg/L)	5.8	5.1	5.4	6.4	7.9	6.2	7.0	9.1	6.9	6.5	7.0	7.4	4.7	4.4	4.4	4.7
	NO_2 (µg/L)	23	28	25	24	28	29	25	29	29	33	23	35	46	76	46	32
	NH_4 (µg/L)	44	34	29	54	28	34	30	53	32	27	22	63	105	91	40	89
	DON (mg/L)	1.4	0.9	1.2	1.6	1.6	1.1	1.3	1.9	1.6	1.0	1.3	1.7	1.3	0.9	1.2	1.4
	TDN (mg/L)	7.3	6.0	6.6	8.1	9.6	7.3	8.4	11.1	8.6	7.6	8.3	9.3	6.2	5.4	5.7	6.2
	TPN (mg/L)	0.1	0.4	0.1	0.1	0.1	0.1	0.2	0.4	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.1
	TN (mg/L)	7.3	6.0	6.5	8.0	9.6	7.2	8.3	11.0	8.5	7.5	8.2	9.1	6.1	5.3	5.7	6.2
Phosphorus Species	PO_4 (µg P/L)	37	48	43	42	44	85	80	72	63	138	128	71	167	212	192	95
	DOP (µg P/L)	8	10	10	9	13	15	12	12	12	19	18	12	17	59	17	13
	TDP (µg/L)	44	53	46	50	55	91	85	79	77	135	130	80	172	238	182	107
	TRP (µg/L)	51	70	52	53	57	94	83	82	93	165	169	92	107	176	117	75
	TPP (µg/L)	27	24	28	35	19	21	34	25	23	16	52	31	59	55	87	49
	TP (µg/L)	70	73	73	83	69	112	119	104	98	147	181	109	231	283	269	148
	TDP:TPP	2.6	2.7	2.6	3.5	6.8	13.4	5.4	4.9	4.3	15.3	5.9	4.1	4.4	6.9	3.5	2.0
	PO_4:B	1.7	2.3	1.7	2.8	1.3	3.2	2.7	4.0	3.7	6.8	4.6	4.6	6.5	8.7	5.5	6.4
	TDN:TDP	166	113	143	162	175	80	99	141	112	56	64	116	36	23	31	58
Carbon	DOC (mg/L)	5.3	3.7	4.7	5.8	4.5	3.9	5.0	4.8	5.1	4.2	3.8	6.1	7.0	5.1	5.4	6.7
	DOC:DON	4.3	3.9	3.0	3.2	3.3	3.7	2.5	2.1	3.3	3.6	2.1	2.8	5.1	5.7	3.6	4.1
	DOC:DOP	491	539	436	476	442	591	354	356	432	658	308	430	933	255	394	420
Ions	Al (µg/L)	42	31	28	55	71	31	29	51	66	40	24	52	70	27	26	50
	B (µg/L)	26	26	33	32	32	31	46	28	24	26	33	40	27	31	34	31
	Ca (mg/L)	127	129	142	130	134	132	143	138	122	120	131	123	132	128	139	128
	Cl (mg/L)	39.1	39.0	39.9	40.6	44.4	44.7	44.0	53.1	42.5	43.6	44	43.2	46.4	50.8	48.2	45.1
	Fe (µg/L)	55	47	57	38	38	35	51	33	44	40	46	37	61	57	67	46
	TSS (mg/L)	8.0	5.3	6.1	7.8	4.6	6.1	8.7	5.7	4.1	3.4	2.7	5.1	7.4	8.7	10.1	5.8

Table 3: Assessing the ability of nutrient concentrations to differentiate between four classifications of wastewater treatment plant via the Kruskal–Wallis *H*-test and linear discriminant analysis.

Variable	Kruskal-Wallis		Linear Discriminant Analysis			
	H-value	*p* value	Selection step	Wilks-Lambda	*p* value	Cumulative % of samples correctly classified
NO_3	117.2	<0.001	1	0.8527	<0.001	44.0
NO_2	69.9	<0.001	2	0.7356	<0.001	44.7
TRP	105.8	<0.001	3	0.6847	<0.001	48.1
PO_4	122.2	<0.001	4	0.6586	<0.001	48.3
TP	114.6	<0.001	5	0.6438	0.003	48.3
DOP	16.5	<0.001	6	0.6285	0.002	49.3
TDP:TPP	78.8	<0.001	7	0.6181	0.016	49.3
NH_4	68.4	<0.001	8	0.6104	0.052	49.5
TPN	4.4	0.223	9	0.6057	0.186	49.5
TDP	139.2	<0.001	10	0.6048	0.835	49.6
TPP	57.1	<0.001	11	0.6028	0.555	50.5
DON	16.9	<0.001	12	0.6022	0.912	51.1
TN	101.3	<0.001	13	0.6012	0.786	51.1

Table 4: Calculated economic damage costs of nutrient enrichment in the River Wensum at site 18. Values in parentheses reflect the uncertainty range in the 2014 pollutant prices assigned by the UK government.

Parameter	Load (kg year^{-1})	Pollutant price (£ kg^{-1})	Damage cost (£ year^{-1})
TN	863,917	0.43 (0.24-0.62)	371,484 (207,340 – 535,628)
TP	12,037	12.79 (2.77-22.66)	153,953 (33,342 – 272,758)
TSS	629,443	0.054 (0.047-0.061)	33,989 (29,584 – 38,396)
		Total	559,426 (207,266 – 846,782)

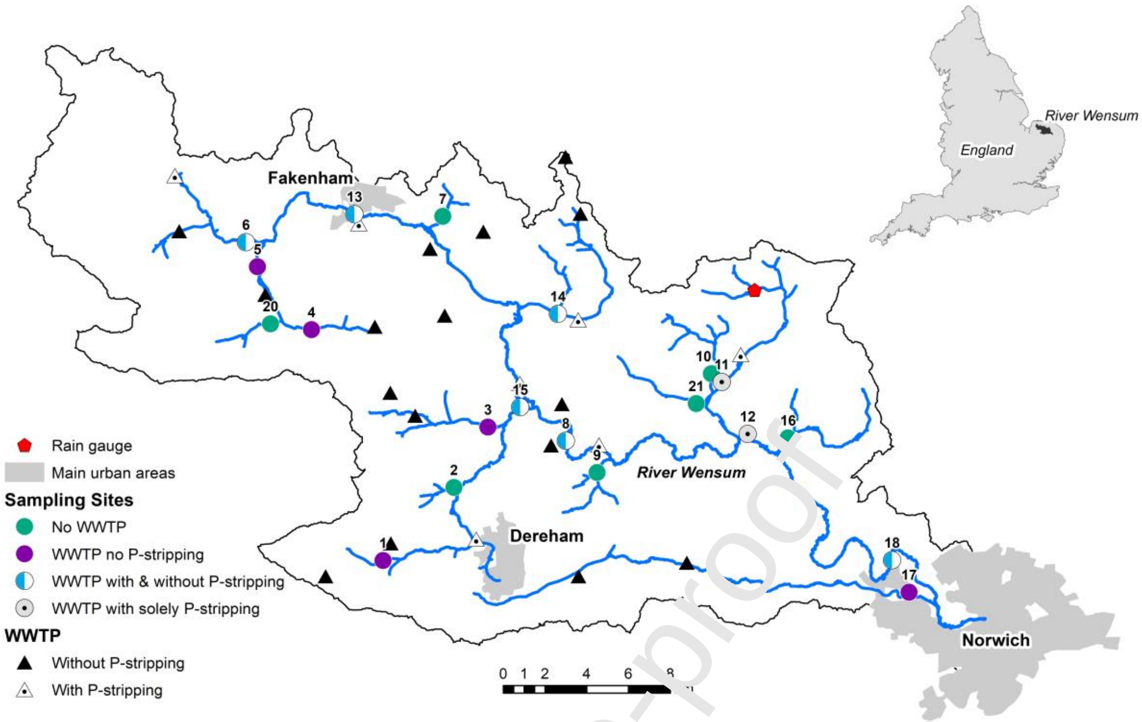
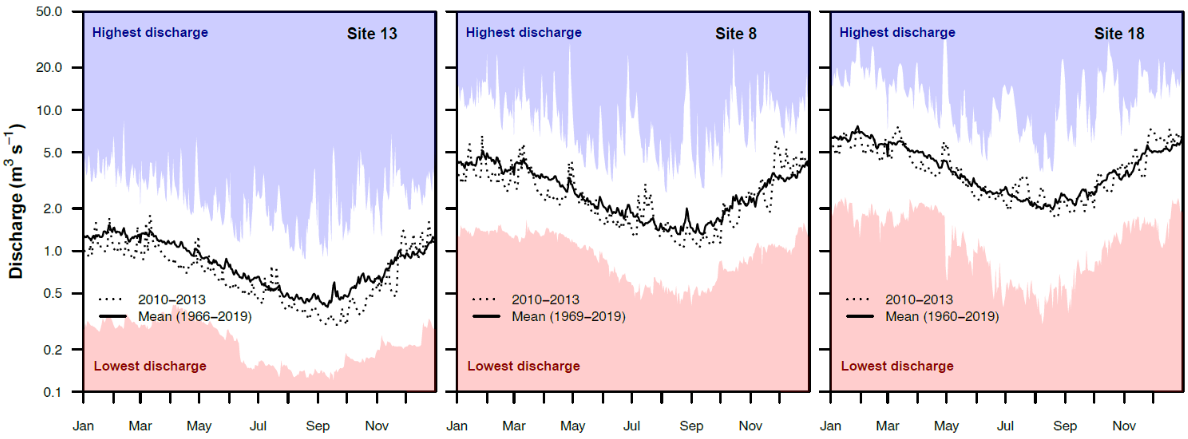

Fakenham
Dereham
Norwich
River Wensum
England
River Wensum
Rain gauge
Main urban areas
Sampling Sites
No WWTP
WWTP no P-stripping
WWTP with & without P-stripping
WWTP with solely P-stripping
WWTP
Without P-stripping
With P-stripping
0 1 2 4 6 8

Fig. 1



Discharge (m^3 s^{-1})
50.0
20.0
10.0
5.0
2.0
1.0
0.5
0.2
0.1
Highest discharge
Site 13
2010–2013
Mean (1966–2019)
Lowest discharge
Highest discharge
Site 8
2010–2013
Mean (1969–2019)
Lowest discharge
Highest discharge
Site 18
2010–2013
Mean (1960–2019)
Lowest discharge
Jan
Mar
May
Jul
Sep
Nov

Fig. 2

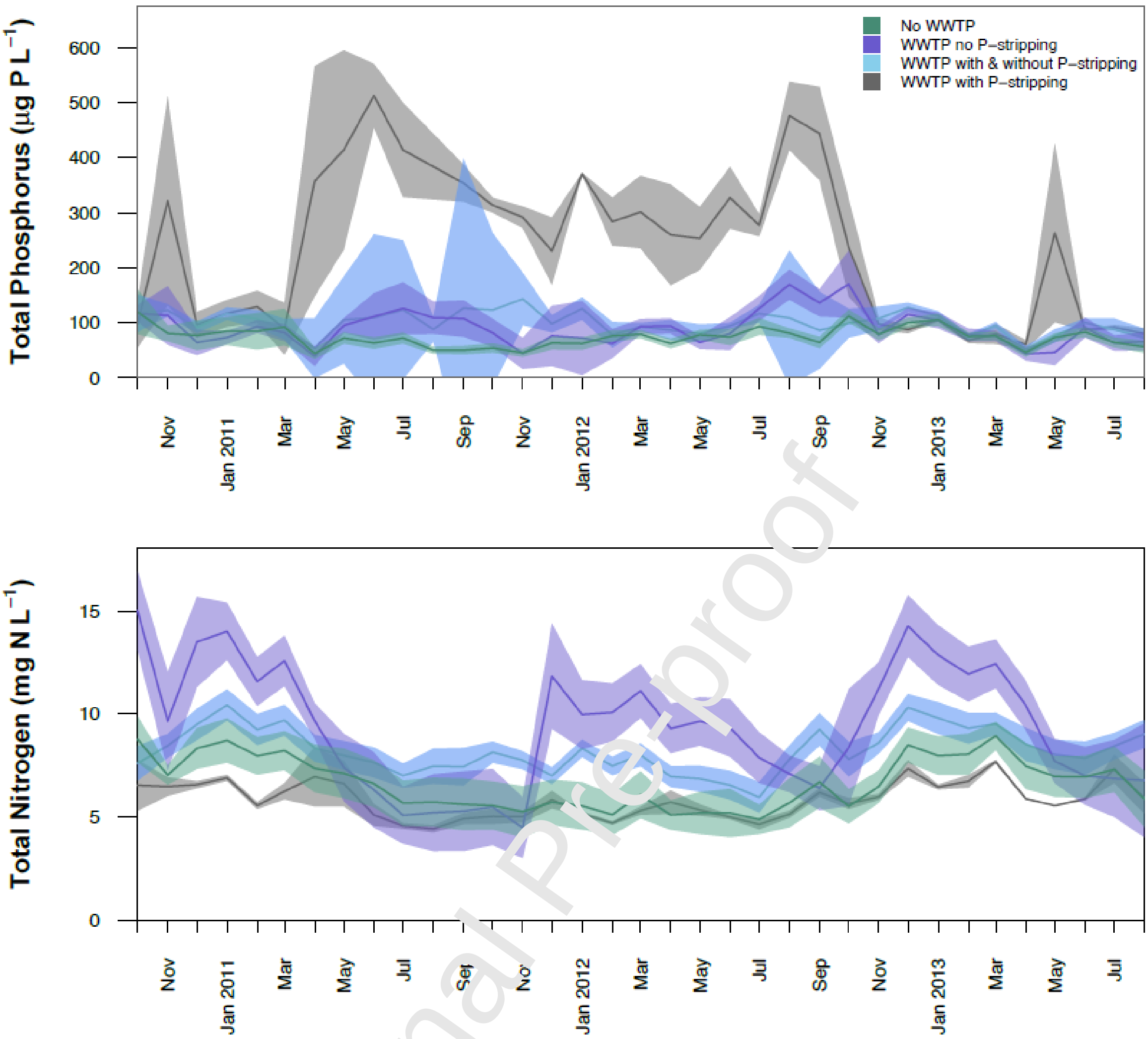
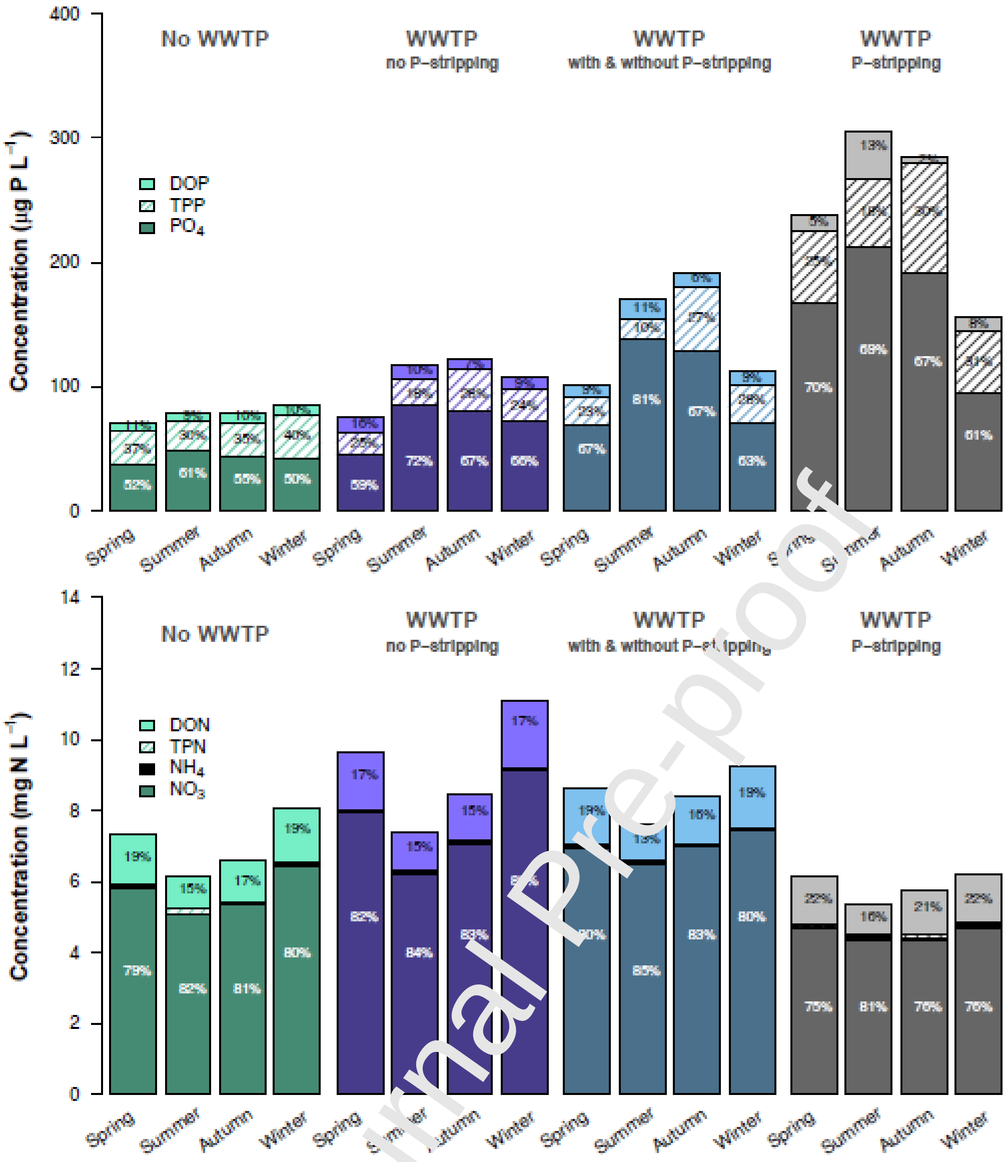

Total Phosphorus (µg P L⁻¹)
600
500
400
300
200
100
0
No WWTP
WWTP no P–stripping
WWTP with & without P–stripping
WWTP with P–stripping
Nov
Jan 2011
Mar
May
Jul
Sep
Nov
Jan 2012
Mar
May
Jul
Sep
Nov
Jan 2013
Mar
May
Jul
Total Nitrogen (mg N L⁻¹)
15
10
5
0

Fig. 3



Concentration (µg P L⁻¹)
No WWTP
WWTP
no P–stripping
WWTP
with & without P–stripping
WWTP
P–stripping
DOP
TPP
PO4
Spring
Summer
Autumn
Winter
Concentration (mg N L⁻¹)
DON
TPN
NH4
NO3

Fig. 4

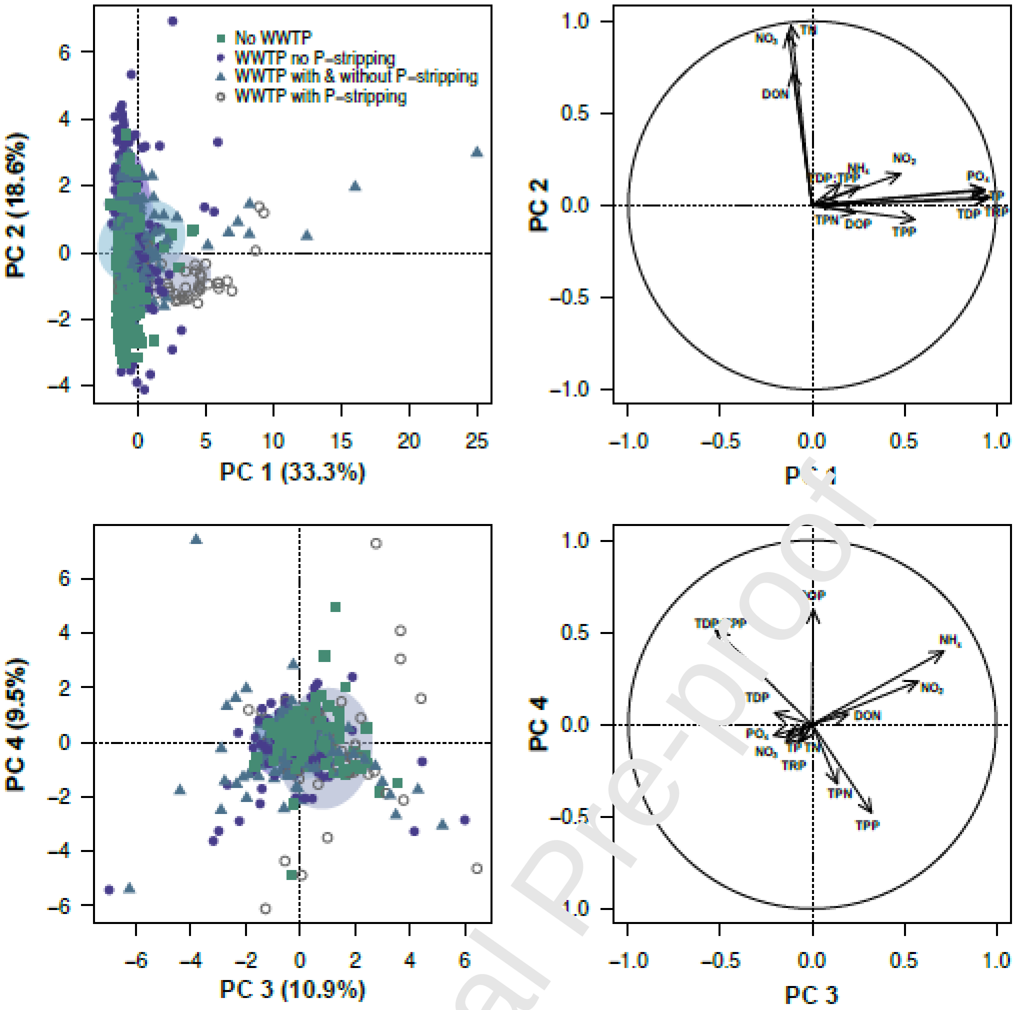

No WWTP
WWTP no P-stripping
WWTP with & without P-stripping
WWTP with P-stripping
PC 1 (33.3%)
PC 2 (18.6%)
PC 3 (10.9%)
PC 4 (9.5%)
PC 1
PC 2
PC 3
PC 4
DON
TN
TPN
DOP
TPP
TP
TRP
TDP
NH4
NO3
NO2
PO4

Fig. 5

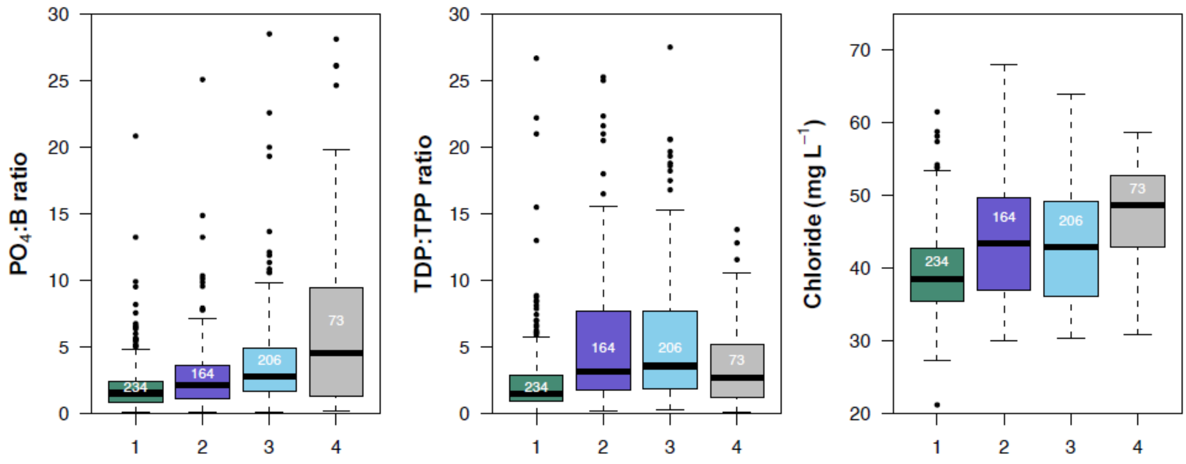


Fig. 6

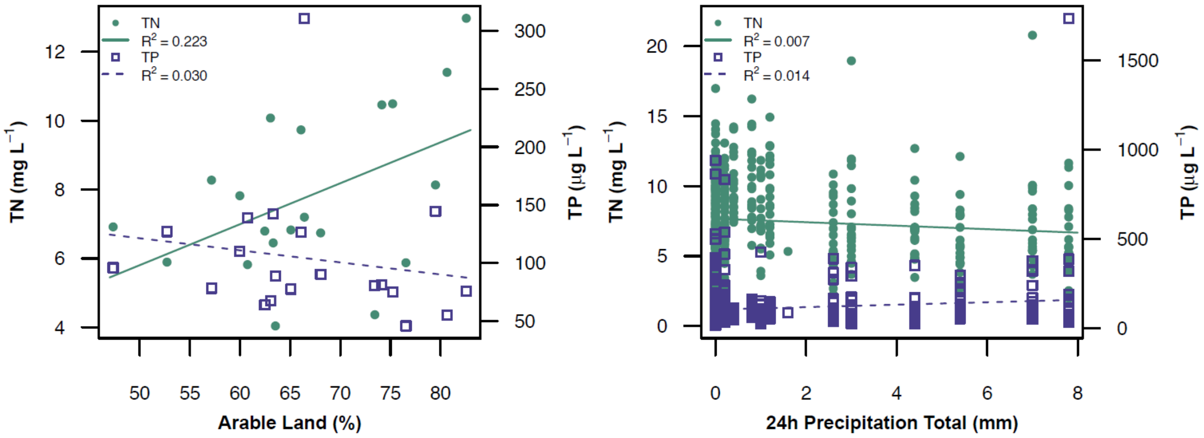

TN
$R^2 = 0.223$
TP
$R^2 = 0.030$
TN (mg L^{-1})
TP (µg L^{-1})
Arable Land (%)
TN
$R^2 = 0.007$
TP
$R^2 = 0.014$
TN (mg L^{-1})
TP (µg L^{-1})
24h Precipitation Total (mm)

Fig. 7

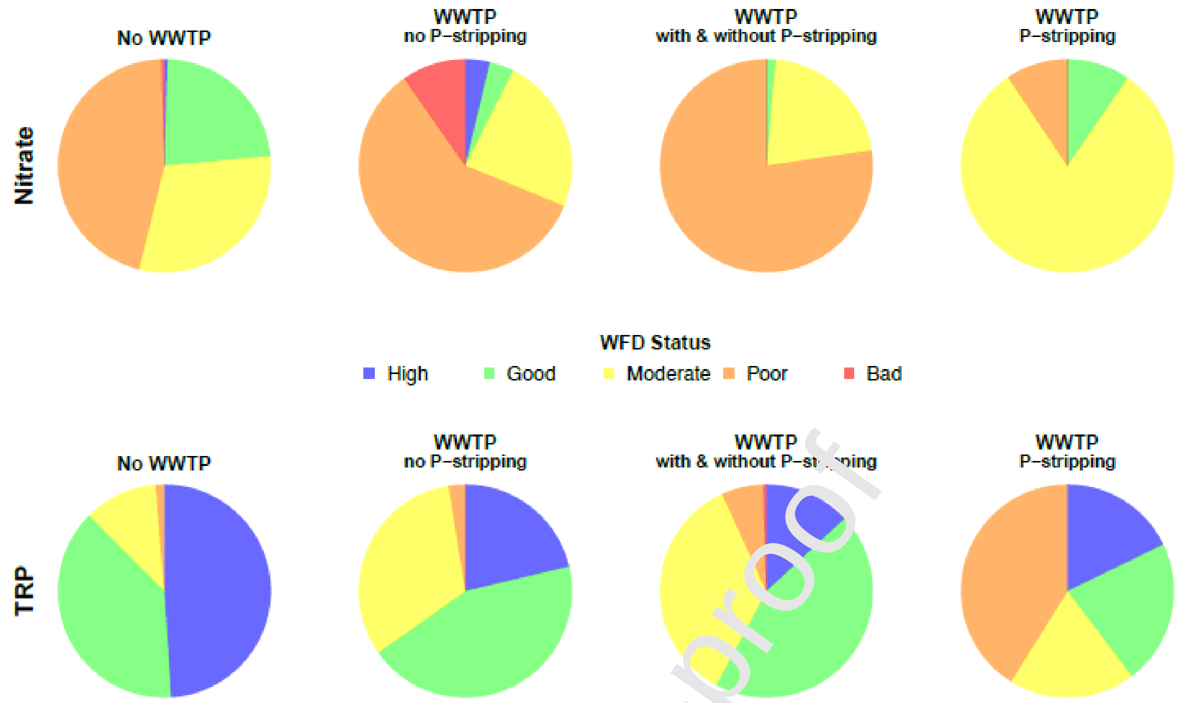

Nitrate
TRP
No WWTP
WWTP no P–stripping
WWTP with & without P–stripping
WWTP P–stripping
WFD Status
High
Good
Moderate
Poor
Bad

Fig. 8

Credit Author Statement

Richard Cooper – Conceptualization; methodology; formal analysis; investigation; data curation; writing – original draft; visualization.

Richard Warren – Investigation; formal analysis; writing – original draft

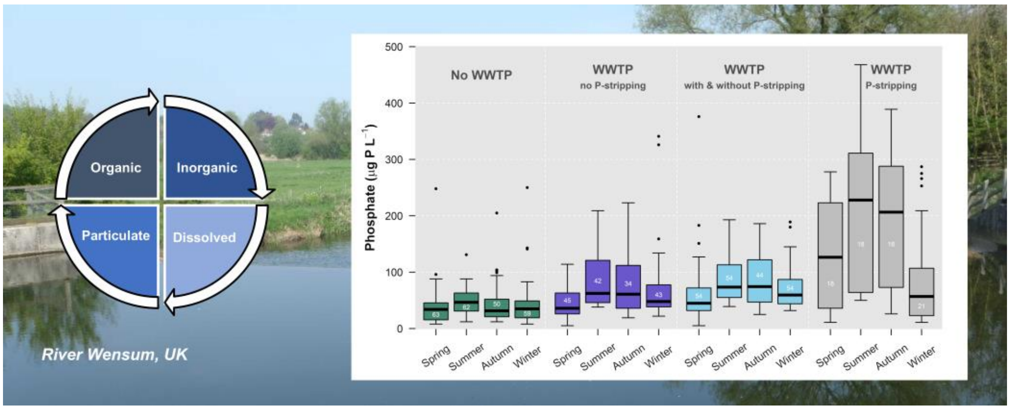
Sarah Clarke – Investigation; formal analysis; writing – original draft

Kevin Hiscock – Project administration; funding acquisition; writing – review & editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Graphical abstract

Highlights

- Impacts of sewage effluent on nutrient dynamics across River Wensum assessed;
- Four contrasting locations of wastewater treatment plant (WWTP) classified;
- Overlaps in nutrient composition made differentiating classifications difficult;
- Tertiary treatment did not reduce phosphorus concentration downstream of WWTPs;
- Elevated nitrate concentrations were primary reason for poor hydrochemical status;