Science of the Total Environment 927 (2024) 171958

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Hydrodynamics and phosphorus loading in an urbanized river channel influences response to future managed change: Insights from advection-dispersion modelling

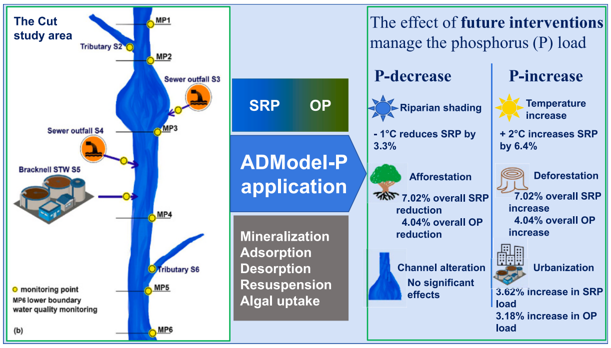
Mihaela Borota[a], Elisabeta Cristina Timis[a,*], Michael George Hutchins[b], Vasile Mircea Cristea[a], Mike Bowes[b], James Miller[b]

[a] Babes-Bolyai University, Department of Chemical Engineering, Computer Aided Process Engineering Research Centre, 11, Arany Janos, 400028 Cluj-Napoca, Romania
[b] UK Centre for Ecology and Hydrology Wallingford, Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB, UK

HIGHLIGHTS

- Analysing transformation fluxes is essential in formulating mitigation measures.
- Temperature has bigger effects on phosphorus during winter than in summer.
- Changes in controlling parameters will affect the entire river stretch.
- Afforestation and deforestation affect a shorter river length than other measures.
- The STW effluent affects a longer river length.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: JV Cruz

Keywords:
Phosphorus in-river transformations
Water quality model
Pollution mitigation
Phosphorus load
Nature-based solutions
Afforestation

ABSTRACT

There is a need to understand what makes certain targeted measures for in-river phosphorus load reduction more effective than others. Therefore, this paper investigates multiple development scenarios in a small lowland polluted river draining an urban area (The Cut, Bracknell, UK), using an advection-dispersion model (ADModel-P). A comparative analysis is presented whereby changes in concentrations and fluxes of soluble reactive phosphorus (SRP) and organic phosphorus (OP) have been attributed to specific transformations (mineralization, sedimentation, resuspension, adsorption-desorption, and algal uptake) and correlated to controlling factors. Under present day conditions the river stretch is a net source of SRP (10.4 % increase in mean concentration) implying a release of previously accumulated material. Scenarios with the greatest impact are those based on managed reduction of phosphorus load in sources (e.g., 20 % increase in afforestation causes an in-river SRP and OP reduction of 1.3 % to 12.6 %) followed by scenarios involving changes in water temperature (e.g., 1 °C decrease leads to in-river SRP reduction around 3.1 %). Measures involving increased river residence time show the lowest effects (e.g., 16 % decrease in velocity results in under 0.02 % in-river SRP and OP reduction). For better understanding downstream persistence of phosphorus pollution and the effectiveness of mitigation

---

* Corresponding author.
E-mail address: elisabeta.timis@ubbcluj.ro (E.C. Timis).

https://doi.org/10.1016/j.scitotenv.2024.171958
Received 31 March 2023; Received in revised form 15 February 2024; Accepted 23 March 2024

measures the research demonstrates the importance of establishing when and where reaches are net adsorbers or desorbers, and whether sedimentation or resuspension is important.

1. Introduction

Recent evidence reveals a continuing vulnerability of rivers worldwide, due to problems attributed to elevated nutrient loads, including phosphorus, in the context of anthropogenic pressure, land-use change and effects of climate change (Angello et al., 2021; Guo et al., 2019; Mack et al., 2019). Investigations on mitigation measures predict positive effects of the riparian shading increase, technical improvements, agricultural extensification (Mack et al., 2019), forest land increase, infiltration basins (Fonseca et al., 2018), water reservoirs (Gruss et al., 2021), vegetation restoration (Xin et al., 2019) and self-purification enhancement (Babamiri et al., 2021). A combination of measures may be needed in highly polluted rivers, as reduction in point source pollutant load (such as wastewater recovery facilities or polluted tributaries) alone have proved to be insufficient (Angello et al., 2021). It is noted, though, that precipitation, wet periods, and intensification of land use (such as extending impervious surfaces in developed areas, and agricultural activities) may offset the benefits of these purposeful management actions aimed to reduce the in-stream phosphorus load (Ryberg et al., 2018). Also, the impervious surface increase correlates with increased runoff volume and water quality degradation (Fonseca et al., 2018). On the other hand, during dry warm months, nutrient release processes are significantly dominant at catchment scale (Gruss et al., 2021).

A common emphasis is the critical need to implement targeted measures to reduce the anthropogenic stress on waterbodies, which would decrease the nutrient load originating outside the stream. Notably and especially in urbanising catchments, the role of Nature-based Solutions for improving water quality amongst other environmental indicators is increasingly recognised; with a need to understand what level of interventions is required and whether effects are exclusively local or if more widespread consequential benefits are achievable downstream (Hutchins et al., 2021). In this context a series of opportunities are emerging. Firstly, there is a need to improve understanding of causal factors in the realm of long-term behaviour and impact (Wong et al., 2018), such as urban factors (Angello et al., 2021; Ryberg et al., 2018), suspended particulate matter (Ji et al., 2022), soil moisture, antecedent period streamflow, vegetation cover or water temperature (Guo et al., 2019), considering the relationship of such factors with climate change (Zhang et al., 2021). Further, the means to manipulate these factors should be proposed as part of pollution mitigation measures. For this, an essential step is the comprehension of pollutant fate in the river system because it facilitates understanding what makes certain mitigation measures more effective than others. From this perspective, in relation to phosphorus, some of the specific knowledge gaps are: (i) understanding and estimation of adsorption-desorption, (ii) the relation between adsorption and algal blooms, (iii) the representation of event fluxes. In these directions a high modelling resolution would reveal more knowledge (e.g., Determan et al. (2021) underline the importance of high-frequency data for algal bloom control) and would help identify if any lack of knowledge thereof hinders the selection of the best pollution mitigation and water quality improvement measures (e.g., Acuña et al. (2019) demonstrated that high-frequency monitoring will improve the best management practices).

A high temporal and spatial resolution model for in-river P transport (ADModel-P, Timis et al. (2022)) has been successfully developed for the fast-flowing rural upland River Swale, England where results show that transformation processes are an important contributor to in-river P dynamics. The model showed conversion of OP to SRP via mineralization to be very important in River Swale, together with sedimentation, resuspension, uptake, and adsorption-desorption. As driven by readily-available data, there is scope to apply ADModel-P elsewhere, because the need for a better understanding of in-stream nutrient dynamics is sustained by strong arguments in multiple studies, such as Kranji reservoir in Singapore (Chua et al., 2012), Severn River in UK (Parsaie and Haghiabi, 2017), urban streams in Melbourne, Australia (Imberger et al., 2011), the Oliwski Stream, Poland (Matej-Lukowicz et al., 2020) or The Cut, Bracknell (Halliday et al., 2015; Wade et al., 2012). Although rarely problematic in rivers such as the Swale, algal blooms are widespread worldwide and it is important to modify the modelling approach to better account for its contribution. In this way the ADModel-P approach is well-placed to fully represent the interplay between nutrient sources, mitigation actions and the progressive downstream development of pollution impacts and their abatement through intervention. On a wider extent, advection-dispersion models and especially the detailed spatial-temporal approach (such as the application of ADModel-P), which became less common during latest years, may help in-depth investigations in the above-mentioned case studies, targeting directions discussed by Timis et al. (2022), which also mention valuable recent studies. Advection-dispersion modelling improved the modelling performance even in the case of complex scenarios, such as branch- or loop-type river networks (Fardadi Shilsar et al., 2023).

The Cut is a heavily impacted system that receives approximately 50 % of its annual P catchment load from urban discharges (Halliday et al., 2015). The Cut river channel is typical of an urban modified channel (e.g., concrete river bed), degraded and disconnected from floodplains (reviewed by McGrane, 2016) and for example conceptualized by (Walsh et al., 2005) the urban stream syndrome. Generally, nutrients (including SRP and OP) and other pollutants are likely to have elevated concentrations in urban rivers. Due to high nutrient concentrations The Cut status is classified as “poor” by the EU Water Framework Directive and there is ecological vulnerability of anoxia under increases in organic loading, water temperature, or urban expansion (Halliday et al., 2015). Moreover, Wade et al. (2012) emphasize the complexity involved in managing and designing efficient P-reduction strategies. The Cut is a relevant case study for point-source dominated rivers, highly affected by human effluents. The capacity for retention or release of P in channels is related to both the long-term loading of P from upstream sources (e.g., effluents) and the geochemical composition of the bed sediment (e.g., presence of suitable binding sites for adsorption, more specifically binding to iron or aluminium oxides, and co-precipitation with calcite). This can then be related to findings from monitoring studies identifying where and when riverbeds act as sources or sinks (e.g., Jarvie et al., 2005; Halliday et al., 2015). By deepening its understanding, valuable insight is gained for catchments that face similar pressures.

In this context the present research seeks to understand the in-river behaviour of inorganic and organic phosphorus (SRP and OP), including transformations and fluxes of in-stream sinks and sources. The objectives of this research are (1) the application of ADModel-P (detailed Advection-Dispersion Model for in-river phosphorus transport, Timis et al. (2022)) for The Cut, in order (2) to analyse several methods for the reduction of the in-river phosphorus load, and (3) identify the most effective methods by understanding the behaviour of SRP and OP.

2. Study area and field data

The Cut is situated on south-east England and drains an area of 124 km^2 (Fig. 1a). It flows north-eastwards from Bracknell, where the headwaters are situated, and joins the Thames. In the middle and lower reaches of The Cut significant input of treated sewage effluent is received in the main channel (at Bracknell, Ascot, and Maidenhead) and via the tributaries (Halliday et al., 2015; Wade et al., 2012). The investigated stretch is located mainly in the middle section, between Frampton's Bridge, Binfield Road (MP1, Fig. 1b and Supplementary Table S1), and Paley Street (MP6), measures 8.19 km length and contains 11 monitoring points: 6 in the mainstream (MP1 to MP6) and 5 in the tributaries and point sources (S2 to S6). The stretch was divided into 5 reaches (R1 to R5). Its typical parameters are presented in Fig. S1.

The field data consists of a 12-month time series (October 2013–September 2014) for the water flow, water temperature, and radiation, at hourly resolution, plus concentrations of OP and SRP at a lower resolution (Supplementary Fig. S1). At MP6 samples have a weekly frequency, while at MP1 and in other sites the resolution is lower (monthly). For the four tributaries and the storm sewer outfall, the water flow was available as time series, whereas in the absence of comprehensive data the SRP and OP concentrations were considered constant. In the case of Bracknell STW, the OP and SRP concentrations were collected fortnightly while the water flow are more frequent, containing daily observations throughout 2014.

3. Methodology

ADModel-P has been calibrated and verified for The Cut, and further used to simulate eight scenarios involving modified controlling factors and phosphorous sources, to illustrate possible river development. A comparative analysis has been performed and results presented.

3.1. ADModel-P background

ADModel-P (Timis et al., 2022) uses an analytical solution for the one-dimensional advection-dispersion equation, to describe the phosphorus dynamic transport along a river in the case of continuous point discharge from multiple point sources. The ADModel-P architecture is captured in Supplementary Fig. S2. Inputs consist of parameters describing the river channel (e.g., channel width, river bed slope, location of sources and monitoring points) and variables expressing controlling factors (e.g., water flow, water temperature, seasonality) along with the SRP and OP concentrations measured at MP1, in the tributaries and at the sources. Outputs consist of concentrations of SRP and OP along the river at a space resolution of 40 m and a time resolution of one hour. The proposed set of transformations considered to explain the variation of SRP and OP are mineralization, sedimentation, resuspension, algal uptake, and adsorption-desorption. Process rates are of zero or first order to SRP and OP (depending on transformation), with rate constants estimated using a set of empirical coefficients (noted with M and R) to express the rate constant dependency on controlling factors (water temperature, water flow and seasonality). This transformations model will be transposed to The Cut from the River Swale application (Timis et al., 2022) by calibrating the empirical coefficients (M and R) for mineralization, sedimentation, resuspension, and adsorption-desorption, while the algal uptake will be expressed in a newly modified manner. The SRP uptake estimations rely on the solar radiation, water temperature and SRP concentration as controlling factors for the net algal growth rate, the Chlorophyll-a concentration, and the nutrient fraction in the algae cells (α, assumed to remain constant throughout the year). The net algal growth rate results after gross algal growth rate undergoes excretion, dark respiration and photosynthesis, and mortality. These processes are expressed in relation to the controlling factors through an optimum curve model. This approach implies an optimum value for temperature, solar radiation, and SRP concentration which if not attained or surpassed, will result in an inhibiting effect of the respective process. In this way, the aforementioned factors limit or accelerate the algal uptake. All constraints for the assumed biological transformations were defined using values from previous research (Bowie et al., 1985; Kowe et al., 1998).

Considering the spatial variability of phosphorus compounds transformations in relation to the river channel and environmental parameters heterogeneity it may be reasonable to argue the opportunity of a 2D model application, which would capture the cross-section variability as well, compared to a 1D model. The calibration of a 2D model involves all field data the 1D model needs, plus measurements across the channel (e.g., for concentration, temperature) and the estimation of cross-section profiles of key parameters (e.g., velocity, dispersion coefficients). The

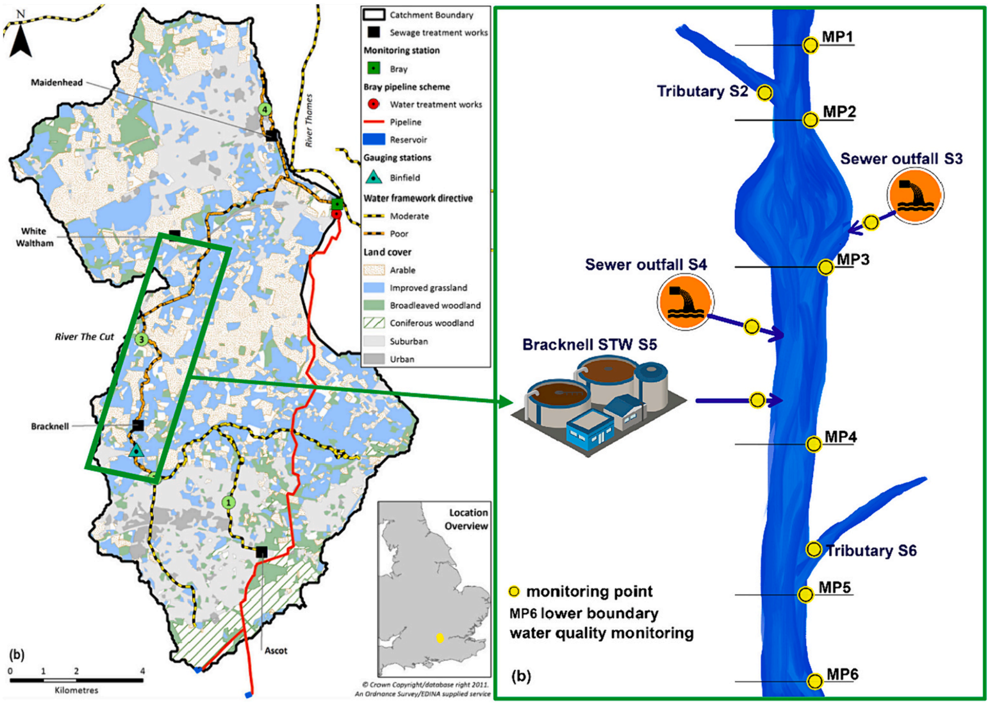


Fig. 1. The Cut Catchment (a, from Halliday et al., 2015) and the simplified conceptual representation of the study area (b). The Cut stretch under investigation is marked with the green box.

above-presented field data for The Cut allowed the confident application of a detailed 1D model, easy transferable to other river stretches, to allow investigating how the urban river subjected to pollution will answer to pressures. On the other hand, the difficulties related to a 2D model would generate transferability issues related to a 2D approach due to low availability of data in most river stretches.

3.2. ADModel-P calibration to The Cut. Procedure

The field data was split into two independent sets, each comprising continuous time series from all four seasons of the year: 60 % for calibration and 40 % for verification. Initially, the key model parameters, including dispersion coefficient, transformation rate coefficients, water velocity, travel time, and seasonality factor (values offered for The Cut in Supplementary Fig. S1), were estimated according to ADModel-P techniques (Timis et al., 2022). This first estimation of SRP and OP shows relatively satisfactory fit between the predicted concentration and measurements. The Nash-Sutcliffe efficiency (NSE) values of 0.67 (SRP) and 0.42 (OP) for the conservative ADModel-P, indicate its good suitability to The Cut. The NSE values of 0.23 (SRP) and − 0.44 (OP) for the non-conservative ADModel using parameters optimized for River Swale reflects a significant difference between the transformations in the two rivers, indicating the need to calibrate the transformation model for The Cut. Further, during optimization simulations have been compared against field data to identify optimum values of the empirical coefficients for The Cut. The model performance was cross-checked by evaluating the predictions against the set of independent data kept for verification purpose, applying multiple model performance evaluation indexes (Timis et al. (2022)).

3.3. The Cut development scenarios

The output of ADModel-P calibrated for The Cut is further termed the default scenario. From this reference point, eight additional datasets have been generated to reflect development scenarios involving specific changes of controlling factors and the field situation (synthetically represented in Supplementary Table S2).

Scenario 1 considers an increase of 20 % in the planted trees area in the catchment, resulting in a decrease of 12.6 % in the SRP and OP load (as estimated from evidence review of literature: Hutchins et al., 2023) for the upstream input, urban tributaries (Triple Bore, Temple Way), and storm sewer outfall. The P load for Bracknell STW and Jealotts Hill Stream remains unchanged.

Scenario 2 considers the increase of the SRP and OP load by 12.6 % for all sources subjected to change in scenario 1. This scenario represents one of, or a combination of, decrease in the tree coverage in the catchment and an increase in pollution sources.

Scenarios 3 to 5 describe the behaviour of the river in situations of water temperature changing throughout the entire year by +1 °C, +2 °C, and -1 °C respectively. Values of temperature changes have been estimated based on previous findings revealing an increase in rivers water temperature by 1–2 °C in Russia since 1998 (Magritsky et al., 2023) and the projected changes in temperature for 2030 and 2050 up to 2 °C involved in a River Thames suspended sediment transport investigation (Bussi et al., 2016). It is remarked that scenarios 3 to 5 consider only the influence of water temperature change on specific contributions and influences of transformations on the phosphorus load. For a comprehensive analysis on the influence of climate change additional variables must be considered (e.g., such as the factors considered by Bussi et al. (2016)).

Scenario 6 considers the channel widening by 50 % apart from R2 (the widest reach), resulting in a decrease of water depth by 20 % and velocity by 17 %, increasing the residence time (Duró et al., 2016).

Scenario 7 considers an increase in population in the urban area, causing an increase in the Bracknell STW effluent by 20 %, keeping the same SRP and OP concentration levels.

Scenario 8 considers the modifications in the SRP and OP mass flux associated to the STW in the case of severe rainfalls. Over the 10 % exceedance rate (Q10) for the water flow (1.3 m^3/s for The Cut) the sewage water is associated with a higher mass flux of SRP and OP (increased by 100 % to 300 % depending on the water flow), as illustrated in the Supplementary Fig. S3. During scenario 8 events the amount of SRP and OP increases significantly due to additional discharges, non-point sources and STW bypass systems (as STW may be unable to process the entire quantity of water received from the system) or uncontrolled outflows (Suchowska-Kisielewicz and Nowogoński, 2021). In some cases, this water is partially processed (e.g., separation of large solids) and further split in two flows: one to follow the treatment flux in the STW and the other one towards a bypass system to be either stored in large buffer tanks (awaiting the later processing) or directly discharged into the river.

4. Results and discussions

4.1. Results of ADModel-P application to The Cut. Default scenario

During the simulated period of time the performance for SRP is better than OP (Fig. 2 and Fig. 3), according to multiple model performance indices (Nash Sutcliffe efficiency (NSE), Percent bias (PBIAS), Modified coefficient of determination (bR2), Root mean square to observations standard deviation (RSR), and Kling-Gupta Efficiency (KGE) presented in the Supplementary Table S3). Fig. 2 and Fig. 3 show the concentrations of SRP and OP (measured and simulated); their transformations rates and the controlling factors (water flow and temperature).

For both, SRP and OP the performance is improved compared to the previous application of ADModel-P to River Swale, as discussed in Section 4.3. Despite the good NSE values (0.78 for SRP and 0.52 for OP) the model doesn't fully capture the short-term temporal variability especially in mid-summer, early autumn, and winter, with larger relative errors for OP occurring in three occasions (December 2014, April 2014, and August 2014). Also simulated acute high concentrations (e.g., in October 2013 for SRP and in June 2014 for SRP and OP) are not captured by the infrequent periodic monitoring and therefore it is rather difficult to assess the model performance on such occasions. During the event in June 2014 the very high input of OP from sources S5 and S6 (Fig. S9b) is correlated with an increase in temperature (Fig. S1c) cause the sharp increase of mineralization. SRP and OP measurements in the main channel only capture the beginning of the event due to lower monitoring frequency. Though, previous investigations based on high frequency monitoring data (Halliday et al., 2015) provide evidence of similar phosphorus concentration short lift spikes in the summer in The Cut main channel, below S5, which may be a sort of event of the same type ADModel is simulating. On the other hand, previous research identified an upper end of published mineralization rates of 0.088 mg/L h (Prentice et al., 2019), while the peak mineralization rate estimated by ADModel-P in The Cut is 0.013 mg/L h. Better simulation performance occurs during autumn and spring compared to summer and winter. SRP is slightly underestimated at the beginning of winter 2013 and overestimated during the rest of the winter, while OP is either under or overestimated during most of the wintertime, without a clear general tendency. On the other hand, during summer SRP mismatches are less apparent than for OP, which shows maximum underestimation (28 July 2014) and overestimation (16 June 2014) and contributes to the higher value of PBIAS for OP (15.1 %) and RSR value slightly close to the threshold. The greatest mismatches coincide with model estimates of large in-stream OP sources relative to sinks. Resuspension (0.0673 mg/L h on 16 June 2014, respectively 0.0502 mg/L h on 28 July 2014, Fig. 3d), the transformation with the greatest impact on OP, is being boosted by the high seasonality factor (0.943 on 16 June 2014, respectively 0.467 on 28 July 2014) and sedimentation exhibits relatively low values (0.0319 mg/L h on 16 June 2014, respectively 0,0479 mg/L h on 28 July 2014, Fig. 3c).

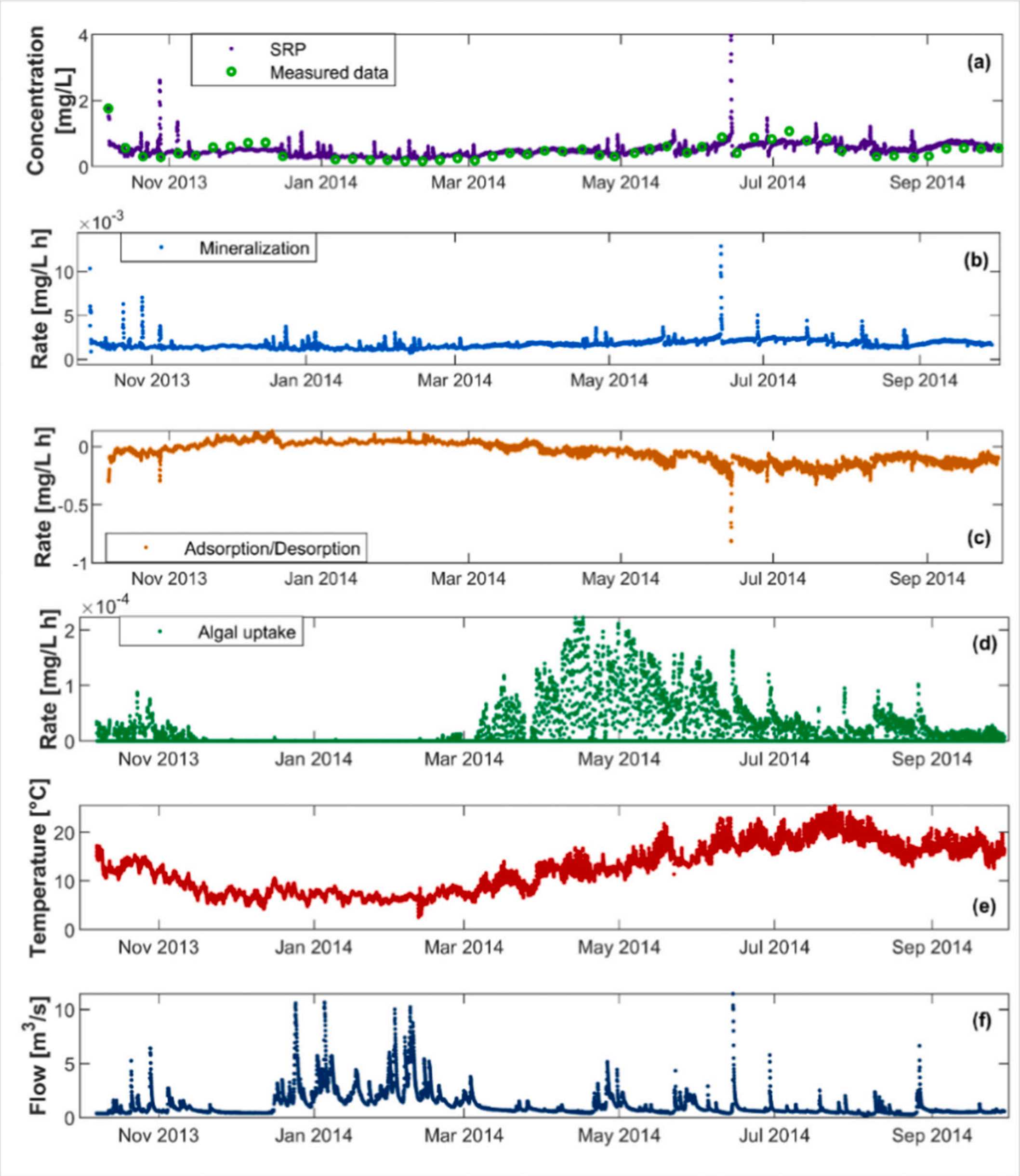


Fig. 2. The simulation of hourly SRP and SRP transformations at MP6 (October 2013–September 2014). (a) SRP concentration: measured and simulated; (b) OP mineralization rate to SRP; (c) SRP adsorption and desorption rate; (d) SRP algal uptake rate; (e) water temperature; (f) water flow.

4.2. Comparative analysis of scenario results

4.2.1. Directions and magnitude of predicted change

Scenario 1, the default scenario, and scenario 2 represent an increasing load gradient. Similarly, scenario 5, the default scenario, scenarios 3 and 4 represent an increasing temperature gradient. For both these stressor gradients, comparative visualisation of quartiles at the monitoring points along the river consistently show linear stressor-impact relationships in the case of SRP and OP (Supplementary Fig. S4). For the load gradient the concentration response is notably steepest (at MP1) for the upper quartile.

The contribution of transformations to the SRP and OP fluxes is consistent across all scenarios (default and possible developments, with values included in Table 1 and visual representation in Supplementary Fig. S5). Resuspension and sedimentation are the main contributors to the variability of OP, while SRP is mainly affected by adsorption-desorption. On the other hand, the conversion of OP to SRP via mineralization has a relatively low impact on OP but an important impact on SRP, compared to the uptake, which has extremely low values compared to all other transformations. Uptake will not be further discussed due to its minimal contribution to the variability of SRP compared to other transformations.

The scenarios with most overall impact on both OP and SRP involve phosphorus load change in the sources (scenarios 1, 2, 7 and 8) (Fig. 4). Scenarios 3, 4 and 5 involving changes in the water temperature have a significant impact on SRP (Fig. 4a), especially via adsorption-desorption. On the other hand, scenario 6, involving an increased residence time (by 16.6 % velocity reduction) due to river widening, exhibits little to no effect on either P species. The mean concentration reduction, under 0.02 % at each MP, is caused by little difference in OP sedimentation and SRP adsorption-desorption (Table 1). To better demonstrate the relative impact of scenario implementation, the net fluxes are presented for adsorption-desorption (Fig. 5 and in Supplementary Fig. S6), while the percentage difference in fluxes is presented for mineralization and sedimentation (Supplementary Fig. S7). Wider discussion in provided further along the paper.

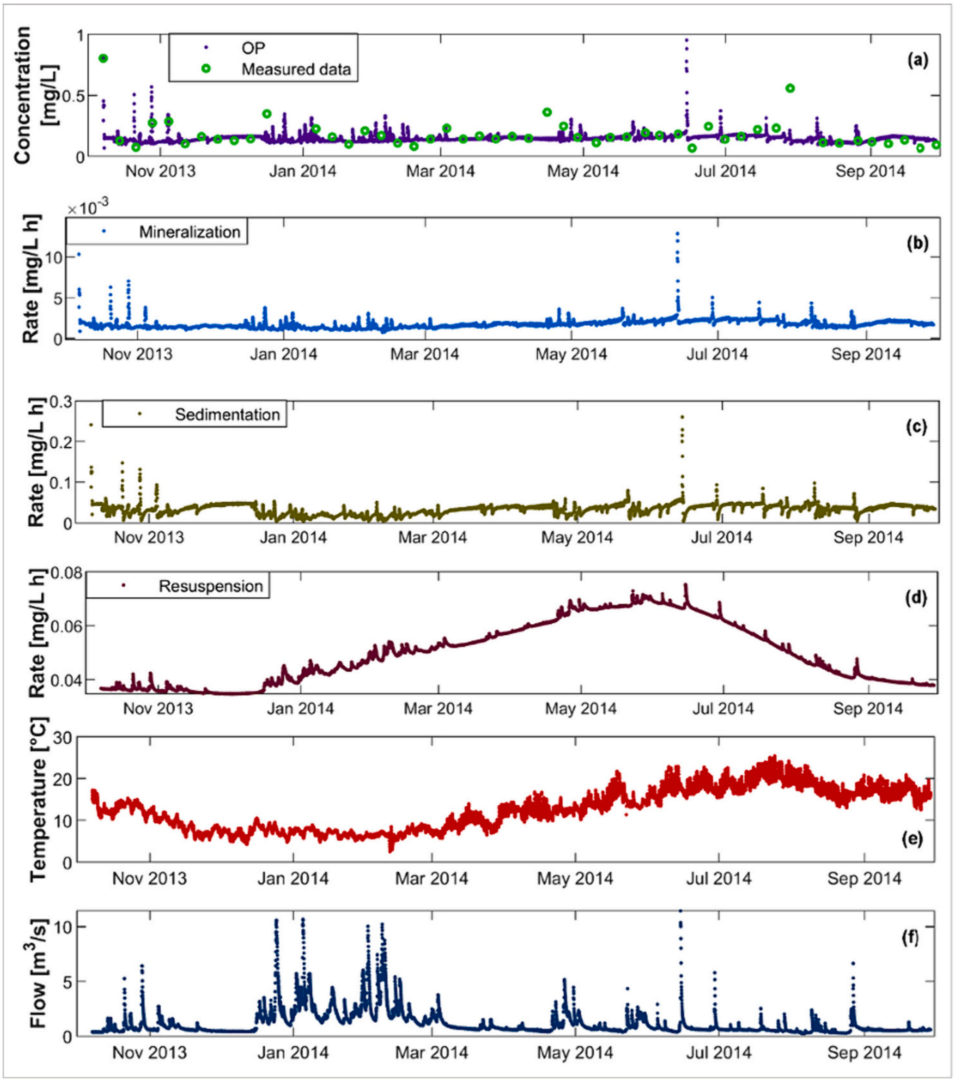


Fig. 3. The simulation of hourly OP and OP transformations at MP6 (October 2013–September 2014). (a) OP concentration: measures and simulated; (b) OP mineralization rate to SRP; (c) OP sedimentation rate; (d) OP resuspension rate; (e) water temperature; (f) water flow.

Table 1
ADModel-P for The Cut: coefficients and transformation rates (positive adsorption–desorption indicates adsorption; negative values indicate desorption).

Variable	Scenario/ Process	Mineralization	Sedimentation	Resuspension	Adsorption-desorption	Algal uptake
Coefficient M	M	0.11	10	0.1	9.27	NA
Coefficient R	R	0	0	0.795	8.26	NA
Rate (MP1 to MP6), mg L-1 day-1	Default	7.50 10^{-3} to 0.31	0.11 to 6.32	0.80 to 1.81	−20.10 to 4.14	2.08 10^{-10} to 7.20 10^{-3}
Mass flux corresponding to the default (calibrated scenario) and each future development scenario for 40 m upstream MP6, kg year^{-1}	Default	56	863	1780	−446	0.42
	Scenario 1	55	852	1780	−433	0.38
	Scenario 2	57	873	1780	−448	0.38
	Scenario 3	58	862	1780	−946	0.41
	Scenario 4	60	862	1780	−1438	0.42
	Scenario 5	54	863	1780	67	0.37
	Scenario 6	56	862	1780	−445	0.38
	Scenario 7	60	920	1864	−543	0.38
	Scenario 8	59	893	1780	−414	0.38

4.2.2. How do temperature and water flow affect downstream impacts of interventions?

In the case of the temperature-controlled scenarios (3–5, and) the lesser impact on OP compared to SRP, happens because temperature-controlled transformations (adsorption-desorption and mineralization) have a greater impact on SRP compared to OP (Fig. 4 and Table 1). The linear variation of SRP is consistent with the temperature change (3.2 % change in concentration for +1 °C to 6.3 % for +2 °C, Fig. 4a) and remains almost constant along the entire river stretch. A decrease in temperature leads to an increase in adsorption (scenario 5 in Fig. 5), while an increase by +1 °C and +2 °C, sets desorption as the predominant process (scenarios 3 and 4). These changes in fluxes are explained

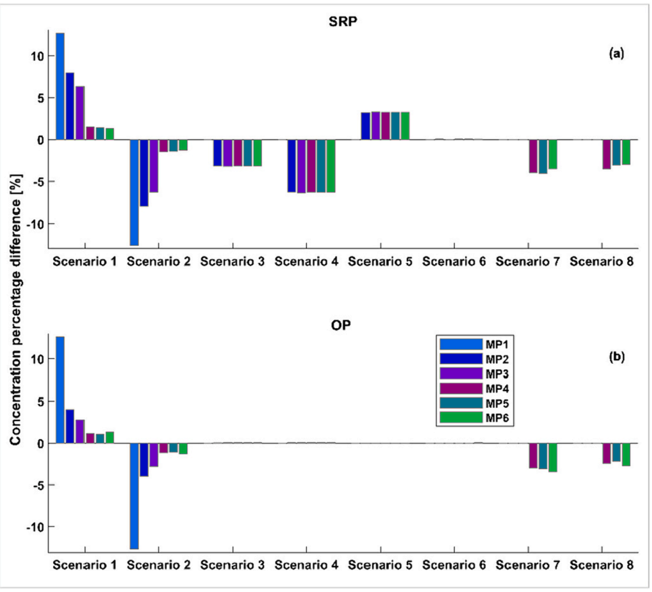


Fig. 4. SRP and OP concentration percentage change at monitoring points (MP) during scenarios: positive values denote reduction; negative values denote increase.

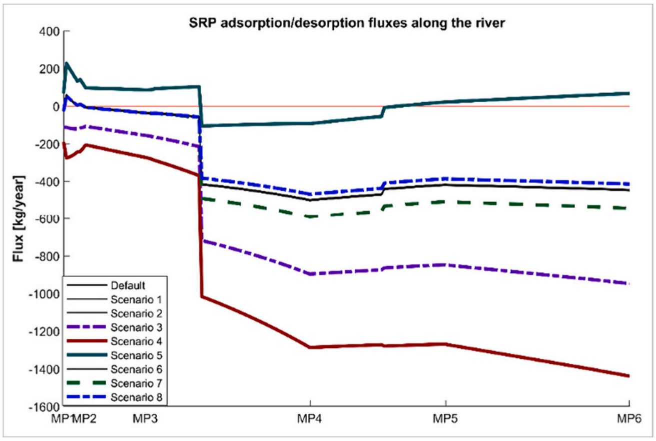


Fig. 5. Adsorption-desorption net flux estimated at a resolution of 40 m.

on one hand, by the temperature influence and on the other hand by the magnitude and the timing of the P load discharges.

4.2.2.1. Adsorption-desorption. The logarithmic dependency of the rate constant to temperature (Supplementary Fig. S8a) is set by the calibrated M and R. For The Cut, R sets 10 °C as threshold temperature between net adsorption and net desorption and M determines the slope (thus, the process magnitude and sensitivity to change). The steeper slope between 0 °C and 10 °C indicates that the most sensitive seasons to a temperature variation for the Cut are the colder ones whereas the warmer seasons are less sensitive. In the default scenario. in R1 the resulting yearly net flux is adsorption, whereas downstream MP2 desorption is dominant and more accentuated (Fig. 5). This is mainly caused by the temporal variation of the P load discharges and the water flows, rather than the effect of temperature alone, as temperature is assumed spatially invariant, because The Cut stretch is relatively short (8.197 km), and temperature measurements were available at MP3 only. Despite the lower winter SRP along R1 (Supplementary Fig. S9), the predominant flux is adsorption due to the high flows occurring. However, this is no longer valid for the lower reaches where desorption predominates. This change is mainly caused by the high P load effluents discharged from Bracknell STW when temperatures are above 10 °C. This switch is readily observed (Fig. 5) as an abrupt drop between MP3 and MP4 at the location of Bracknell STW.

4.2.2.2. Mineralization. The same line of argumentation applies to mineralization. Its dependency to temperature is logarithmic (Supplementary Fig. S8b), and the largest sensitivity is observed between 2.5 °C and 9 °C, during colder seasons. Mineralization at MP1 is the most impacted by temperature change (−4.7 % for scenario 3 and − 8.6 % for scenario 4) and MP4 is the least impacted (−3.8 % for scenario 3 and − 7.3 % for scenario 4), (Supplementary Fig. S7a), due to high winter flows and smaller contribution of sources in the upper reaches compared to lower reaches (Supplementary Fig. S9b). However, at lower reaches fluxes are slightly less sensitive to a temperature change due to the STW's discharges. The same flux variation pattern is maintained for each temperature driven scenario, underlying the effect of sources on the mineralization fluxes.

To summarize, these variations of adsorption-desorption and mineralization explain the bigger effects of changes in water temperature on P concentrations during colder months compared to warmer months.

4.2.3. *Urbanization expansion and phosphorus transformations*

The scenarios regarding modified STW discharged effluent assessed for a population increase (scenario 7) or overflows due to severe rainfalls (scenario 8) highlight the significant impact of this source. Its contribution affects the last two reaches and results in an enrichment of OP, between 2 % to 3.4 % and of SRP, from 3 % to 4 % (Fig. 4).

If the STW effluent flow increases by 20 % due to urbanization (scenario 7), the OP resuspension is also elevated (with 4.7 % to 5.4 % Supplementary Fig. S5), because the water flow (controlling factor for resuspension) modifies. This is the only scenario in which resuspension is affected. The frequent high P load STW discharges during summer boost mineralization (7.4 % to 8.2 %) to higher degree than those of sedimentation (6.3 % and 6.7 %), (Supplementary Fig. S7). The relatively lower sedimentation rates are caused by the increased effluent flows, which reduce in turn the amount of sedimented OP. However, despite the elevated resuspension and lowered sedimentation, the higher STW discharge enriches the river with more SRP compared to OP. This effect is caused by increased desorption and mineralization. In case of increased polluted effluents resuspension, desorption and mineralization are important and particulate P (OP) and SRP are elevated.

Because STW's overflows due to severe rainfalls (scenario 8) occur mainly during cold seasons, the additional P load discharged during these events is mostly adsorbed. This results in a decrease in the yearly adsorption-desorption flux (Fig. 5). Mineralization and sedimentation fluxes are also increased during overflows, but the sedimentation is relatively less affected than mineralization due to the high flows associated to severe rainfalls.

4.2.4. *The spatial effects of interventions*

4.2.4.1. The impact of afforestation and deforestation. Scenarios 1 and 2 reveal how a P load change at the upper reaches (R1 to R3, altogether approximately 1.2 km long) affects the lower reaches (altogether approximately 7 km long). The afforestation in R1 to R3 (scenario 1) showed a reduction in P load of 12.6 % at R1, and progressively lower reductions downstream (Fig. 4), because from R4 downwards the P load of the STW's discharge and the downstream tributaries are not affected by afforestation. Moreover, another important factor that diminishes the impact of changes in P load is the mixing with the downstream higher flows (5 to 10 times higher than in the upper reaches). The effect on the transformation fluxes is a consequent reduction due to adsorption-desorption, mineralization, and sedimentation, being first order with respect to OP and SRP concentration. Decreases in adsorption fluxes at the upper reaches and desorption fluxes at the lower reaches arise (Supplementary Fig. S6). Sedimentation and mineralization fluxes present reduction patterns along the stretch similar to that of OP mean concentration (Fig. 4b). As it is zero order with respect to the OP concentration, resuspension is not affected by the P load change. However, for an increase in the phosphorus input due to deforestation (scenario 2), the response of the river system mirrors the one in scenario 1, displaying the enrichment effect of OP and SRP (Fig. 4).

4.2.4.2. The impact of urban expansion. In contrast, the effects of urban expansion or of overflows are more severe when considering the caused long-distance changes (Fig. 4). The OP and SRP enrichment is 2 to 4 times larger than that for deforestation. This finding is of particular importance for The Cut because it reveals the great impact of Bracknell's STW effluents onto the river system and indicates which and why some mitigation measures involving the STW can be more effective than others.

4.2.4.3. The impact of controlling factors along the entire river stretch. The correlation between temperature and the P load discharges can result in an amplification of a specific type of transformation (e.g., adsorption-desorption), while the water flow has a direct effect on the global magnitude of the process regardless of P concentrations.

In summary, afforestation and deforestation have a greater impact on SRP compared to OP. Upper reaches, where the P load input and the sources are changed due to afforestation and deforestation, are impacted more compared to the lower reaches which are highly influenced by the STW and tributaries, not affected by these measures. The degree of change in the input P load influences the extent to which the river length is affected. Afforestation and deforestation affect a shorter river length, the STW effluent affects a longer river length, and changes in controlling parameters will affect the entire river stretch.

4.3. Comparison with other studies

The relationship between seasonality and nutrients (including phosphorus) has been investigated by Matej-Lukowicz et al. (2020) in two dissimilar catchments from Poland, revealing higher concentrations of total phosphorus (TP) in the small urban catchment, especially during summer (correlated with increased rainfalls causing runoff), compared to the agricultural catchment (where lower concentrations could be caused by dense vegetation and reduced soil erosion). The application of ADModel-P for the urbanized The Cut generally reveals medium range TP concentrations during summer (excepting one occasion of high concentrations correlated with high flows), compared to higher concentrations during autumn and winter. Similarly, the previous application of ADModel-P for the rural River Swale reveals generally lower TP during summer, compared to other times of the year and high concentrations during colder seasons and at high flows. On the other hand, Bol et al. (2018) observed high phosphorus concentrations during summer and increased total annual loads due to high flows during winter in agricultural catchments in Northwest Europe.

The applications of ADModel-P bring significant advance, as the transformation model provides an understanding of the magnitude of each process (mineralization of OP to SRP, sedimentation of OP, resuspension of OP, algal uptake of SRP, and adsorption-desorption of SRP) with the help of process rates and transformation fluxes, facilitating correlations to controlling factors or to possible events or developments in the catchment. Moreover, an improved prediction performance is exhibited for The Cut (e.g., NSE values of 0.76 for SRP and 0.52 for OP), compared to River Swale (0.62 for SRP and 0.47 for OP). Different process rates and fluxes are observed in the two rivers for the simulated periods (Table 2), as well as different extent of relative contribution from each transformation process to the overall SRP and OP dynamics, which reflects the dissimilar nature of the river stretches.

Table 2

Comparative view of SRP and OP fluxes and transformations for River Swale and The Cut during ADModel calibration and evaluation.

	Flux, kg day^{-1} km^{-1}		Rate, mg L^{-1} day^{-1}	
	Swale	The Cut	Swale	The Cut
Mineralization	367	4	0.03 to 2.39	0.0075 to 0.31
Sedimentation	306	59	0.19 to 1.37	0.11 to 6.32
Resuspension	611	122	0.02 to 1.29	0.80 to 1.81
Uptake	181	0.03	0.03 to 0.34	0 to 0.0072
Adsorption-desorption	1747	−30	0.00 to 3.80	−20.1 to 4.14
	Average simulated concentration through the outlet, mg L^{-1} (conservative/ non-conservative)		***Average flux through the outlet, kg day^{-1}***	
	Swale	***The Cut***	***Swale***	***The Cut***
SRP	0.209/ 0.131	0.452/ 0.499	170	41.3
OP	0.149/ 0.145	0.147/ 0.133	310	14.3

The most remarkable differences are the very low contributions of uptake and mineralization in The Cut, while in River Swale mineralization has an important contribution. In both rivers the most prominent transformations are resuspension with respect to OP and adsorption-desorption with respect to SRP, in agreement with Kinouchi et al. (2012) finding that adsorption is likely the dominant phosphate sink in a Japanese river. In River Swale adsorption is predominant across all simulated periods of time, exhibiting larger values at lower temperatures and lower values at higher temperatures, while in The Cut adsorption is more prominent at low temperatures during late autumn to mid-spring (November 2013 to April 2014), and desorption is predominant during the rest of the year (October 2013 and May 2014 to September 2014). In River Swale and The Cut, uptake is the least prominent process. The Cut has far greater relative contribution of point source pollution and shows a higher relative contribution of SRP to TP than the Swale. This is consistent with Aissa-Grouz et al. (2018) who identified a predominant share that the SRP flux has on TP flux in a river dominated by WWTP effluent.

Existing literature also reports values of fluxes for phosphorus only or in correlation to specific sources or processes using field data or models. Below, such findings are compared to our findings.

Jarvie et al. (2005) investigated the interaction of bed sediments with the river water in the Hampshire Avon and Herefordshire Wye catchments using field measurements and a conceptual reach-based model. For 15 locations across these basins mean SRP concentrations varied considerably (12–439 μgL^{-1}). All these sites drained largely rural agriculturally dominated land uses and showed SRP concentrations lower than the Cut but similar to the Swale. Snapshot estimates of SRP fluxes (from sampling campaigns repeated three times) were equated to changes in SRP concentration. Changes in SRP concentration ranged from strong uptake (157 μgL^{-1} in Stretford Brook (Wye)) to slight release (8.1 μgL^{-1} in Ebble (Avon)). In comparison, ADModel-P estimates suggest net SRP uptake of 88 μgL^{-1} in the Swale and net release of 47 μgL^{-1} in the Cut (as derived from Table 2). Release of legacy phosphorus appears more important in the Cut than elsewhere.

Adhikari et al. (2010) reported P fluxes between 22 kg/day and 135 kg/day at the outlet of the watershed for Pike River (Vermont, USA and Quebec, Canada), showing a magnitude between The Cut and Swale (Table 2). Neal et al. (2010) reported SRP fluxes between 0.08 t/year and 497 t/year at four sampling sites in the Thames, the Thame, and the

Kennet (UK). Lower average fluxes are estimated with ADModel at the outlet for The Cut (15.07 t/year) and River Swale (62.19 t/year).

When compared to other research work related to P fluxes ADModel-P is highlighted by (1) the detailed representation of fluxes associated to SRP and OP transformations (mineralization, sedimentation, resuspension, uptake, and adsorption-desorption); (2) the capability to show SRP, OP and transformations fluxes at different space resolution, adjusted to the case study (e.g., 40 m for The Cut and 4.8 km for River Swale); (3) the capability to estimate a total flux for the entire river stretch for SRP, OP and each of the transformations; (4) the capability to correlate these types of fluxes to changes in sources, controlling factors, green and grey developments in the river area. All of this, employing easily attainable field data (e.g., water flow, water temperature).

4.4. Recommendations

The research has served to highlight priorities for further research in The Cut and more widely in other rivers where similar understanding has been gained: (a) focused monitoring to further validate findings (e.g., river bed experiments/mesocosms to quantify adsorption-desorption); (b) focused model calibrations (e.g., ADModel) before/after changes in pollutant loadings and/or at sites along spectrum of pollutant loading which can be insightful for better understanding the magnitude and impacts of legacy pollution; (c) bringing together the modelling approach for phosphorus with simulation of other nutrients (nitrogen and carbon) and therefore making holistic systemic assessments of river ecosystem metabolism and oxygen dynamics in stressed urban rivers; (d) modelling and data-driven analysis of long term (monitoring) and/or large scale (spatially extensive) datasets to understand long term trends and geographical differences in P dynamics; (e) when planning mitigation measures if a specific type of transformation is of interest or it is to be avoided, the ADModel findings from the Cut demonstrate potential for P discharges to be planned based on the predominant transformations of the current season (set by the dependency to temperature) and the water flow (which can reduce the magnitude of processes even if the discharged concentration is high). In this way the river environment can be better protected against the most harmful effects of pollution inputs.

5. Conclusions

This paper described the calibration of ADModel-P to The Cut and the in-stream phosphorus behaviour in cases of future river catchment development scenarios. ADModel brings the possibility to estimate the impact of the P discharges on specific transformation fluxes because it describes the relationship of each of transformation rate to the temperature and water flow as controlling factors. Overall, over a one-year period the model simulated a weekly time-series of observations at the downstream end of an 8.19 km^2 acceptably. Estimates showed that resuspension and sedimentation are the dominant fluxes, and their variability is related to river flow. Net adsorption-desorption is also important: adsorption predominates in winter and desorption in summer, compared to River Swale where adsorption is prominent during all seasons.

The analysis of possible future scenarios made the key findings below.

1. The river is mostly impacted by changes in the phosphorus load in the sources, and afforestation brings significant benefits. These kinds of measures affect SRP and OP, most markedly in reaches where sources are directly contributing. A 20 % increase in afforestation in the first three reaches would lead to SRP and OP reduction between 1 % and 12.6 %. The differences between SRP and OP are due to resuspension (a major contributor to OP variability) not being affected, while adsorption-desorption (the main contributor to SRP variability) only exhibits minimal changes. Only the mineralization and sedimentation fluxes suffer significant modifications in case of afforestation and deforestation.
2. The change in temperature affects SRP very substantially while OP is less affected. A temperature rise would lead to enrichment in phosphorus along the entire river stretch via SRP desorption and OP mineralization to SRP, while the water cooling by 1 °C (e.g., by riparian shading) would lead to lower OP and SRP concentration.
3. Although not involving a projected deterioration in effluent quality, the scenario of increase of sewage discharge due to population increase exhibits a greater detrimental impact on the river phosphorus content than the scenario in which untreated sewage overflow is discharged in the river in periods of major rainfall. Both scenarios increase SRP to a slightly larger extent than OP. The scenario in which river widening is considered shows almost no effect on the SRP or OP concentrations and transformation fluxes.
4. Generally, resuspension and sedimentation are the main contributors to the variability of OP, while SRP is mainly affected by adsorption-desorption. The conversion of OP to SRP is less significant, while the SRP uptake is insignificant.

It has been observed that a thorough analysis of transformation fluxes along the river stretch is essential in the demarche of formulating effective P-reduction measures. In this case using a detailed mathematical model offers an effective and inexpensive method, demonstrating that targeted P-load reduction measures should address decreasing specific phosphorus transformation fluxes by influencing their controlling factors in an effective manner.

CRediT authorship contribution statement

Mihaela Borota: Data curation, Formal analysis, Investigation, Software, Validation, Writing – original draft, Writing – review & editing. **Elisabeta Cristina Timis:** Conceptualization, Formal analysis, Methodology, Resources, Software, Validation, Writing – original draft, Writing – review & editing. **Michael George Hutchins:** Conceptualization, Formal analysis, Investigation, Resources, Validation, Writing – original draft, Writing – review & editing. **Vasile Mircea Cristea:** Resources, Supervision. **Mike Bowes:** Resources. **James Miller:** Resources.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Mihaela Borota reports financial support was provided by The World Federation of Scientists National Scholarship Programme. Mike Bowes and James Miller reports financial support was provided by UK Centre for Ecology & Hydrology Thames Initiative. Mike Bowes and James Miller reports financial support was provided by Natural Environment Research Council. Michael George Hutchins reports was provided by European Union. Michael George Hutchins reports financial support was provided by Joint Programming Initiative Urban Europe. Michael George Hutchins reports financial support was provided by National Natural Science Foundation of China.

Data availability

The weekly water quality data and the sub-hourly hydrological data from urban runoff is available online: Bowes et al. (2020) and Miller and Hutchins (2019). The ADModel-P application to The Cut has been made public (Borota and Timis, 2023).

Acknowledgements

Mihaela Borota acknowledges support from The World Federation of Scientists National Scholarship Programme. Field data has been provided from the UKCEH Thames Initiative under the management of Mike Bowes, the POLLCURB project (funded under the NERC Changing Water Cycle programme, ref. NE/K002317/1) and from the Environment Agency (Bracknell effluent flows). Mike Hutchins acknowledges support from two projects, REGREEN (funded under European Union's Horizon 2020, No.821016) and DeSCIPHER (funded under the Sustainable and Liveable Cities and Urban Areas programme jointly coordinated by the Joint Programme Initiative (JPI) Urban Europe and National Natural Science Foundation of China (NSFC)).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.171958.

References

Acuña, V., Casellas, M., Font, C., Romero, F., Sabater, S., 2019. Nutrient attenuation dynamics in effluent dominated watercourses. Water Res. 160, 330–338. https://doi.org/10.1016/j.watres.2019.05.093.

Adhikari, B.K., Madramootoo, C.A., Sarangi, A., 2010. Temporal variability of phosphorus flux from Pike River watershed to the Missisquoi Bay of Quebec. Curr. Sci. 98, 58–64.

Aissa-Grouz, N., Garnier, J., Billen, G., 2018. Long trend reduction of phosphorus wastewater loading in the seine: determination of phosphorus speciation and sorption for modeling algal growth. Environ. Sci. Pollut. Res. 25, 23515–23528. https://doi.org/10.1007/s11356-016-7555-7.

Angello, Z.A., Behailu, B.M., Tränckner, J., 2021. Selection of optimum pollution load reduction and water quality improvement approaches using scenario based water quality modeling in little Akaki River, Ethiopia. Water 13, 584. https://doi.org/10.3390/w13050584.

Babamiri, O., Vanaei, A., Guo, X., Wu, P., Richter, A., Ng, K.T.W., 2021. Numerical simulation of water quality and self-purification in a mountainous river using QUAL2KW. J. Environ. Inform. 37, 26–35. https://doi.org/10.3808/jei.202000435.

Bol, R., Gruau, G., Mellander, P.E., Dupas, R., Bechmann, M., Skarbøvik, E., Bieroza, M., Djodjic, F., Glendell, M., Jordan, P., Van der Grift, B., Rode, M., Smolders, E., Verbeeck, M., Gu, S., Klumpp, E., Pohle, I., Fresne, M., Gascuel-Odoux, C., 2018. Challenges of reducing phosphorus based water eutrophication in the agricultural landscapes of Northwest Europe. Front. Mar. Sci. 1–16 https://doi.org/10.3389/fmars.2018.00276.

Borota, M., Timis, E.C., 2023. ADModel-P Application to The Cut. HydroShare, Bracknell, UK. http://www.hydroshare.org/resource/531e748ed43d437992ba2286b8fae444.

Bowes, M.J., Armstrong, L.K., Harman, S.A., Nicholls, D.J.E., Wickham, H.D., Scarlett, P. M., Juergens, M.D., 2020. Weekly water quality data from the river Thames and its major tributaries (2009-2017). NERC Environmental Information Data Centre. https://doi.org/10.5285/cf10ea9a-a249-4074-ac0c-e0c3079e5e45.

Bowie, G.L., Mills, W.B., Porcella, D.B., et al., 1985. Rates, constants, and kinetics formulations in surface water quality modeling. EPA 600, 3–85.

Bussi, G., Dadson, S.J., Prudhomme, C., Whitehead, P.G., 2016. Modelling the future impacts of climate and land-use change on suspended sediment transport in the river Thames (UK). J. Hydrol. 542, 357–372. https://doi.org/10.1016/j.jhydrol.2016.09.010.

Chua, L.H.C., Tan, S.B.K., Sim, C.H., Goyal, M.K., 2012. Treatment of baseflow from an urban catchment by a floating wetland system. Ecol. Eng. 49, 170–180. https://doi.org/10.1016/j.ecoleng.2012.08.031.

Determan, R.T., White, J.D., McKenna, L.W., 2021. Quantile regression illuminates the successes and shortcomings of long-term eutrophication remediation efforts in an urban river system. Water Res. 202, 117434 https://doi.org/10.1016/j.watres.2021.117434.

Duró, G., Crosato, A., Tassi, P., 2016. Numerical study on river bar response to spatial variations of channel width. Adv. Water Resour. 93, 21–38. https://doi.org/10.1016/j.advwatres.2015.10.003.

Fardadi Shilsar, M.J., Mazaheri, M., Mohammad Vali Samani, J., 2023. A semi-analytical solution for one-dimensional pollutant transport equation in different types of river networks. J. Hydrol. 619, 129287 https://doi.org/10.1016/j.jhydrol.2023.129287.

Fonseca, A., Boaventura, R.A.R., Vilar, V.J.P., 2018. Integrating water quality responses to best management practices in Portugal. Environ. Sci. Pollut. Res. 25, 1587–1596. https://doi.org/10.1007/s11356-017-0610-1.

Gruss, Ł., Wiatkowski, M., Pulikowski, K., Kłos, A., 2021. Determination of changes in the quality of surface water in the river-reservoir system. Sustainability 13, 1–18. https://doi.org/10.3390/su13063457.

Guo, D., Lintern, A., Webb, J.A., Ryu, D., Liu, S., Bende-Michl, U., Leahy, P., Wilson, P., Western, A.W., 2019. Key factors affecting temporal variability in stream water quality. Water Resour. Res. 55, 112–129. https://doi.org/10.1029/2018WR023370.

Halliday, S.J., Skeffington, R.A., Wade, A.J., Bowes, M.J., Gozzard, E., Newman, J.R., Loewenthal, M., Palmer-Felgate, E.J., Jarvie, H.P., 2015. High-frequency water quality monitoring in an urban catchment: hydrochemical dynamics, primary production and implications for the water framework directive. Hydrol. Process. 29, 3388–3407. https://doi.org/10.1002/hyp.10453.

Hutchins, M.G., Fletcher, D., Hagen-Zanker, A., Jia, H., Jones, L., Li, H., Yu, S., 2021. Why scale is vital to plan optimal nature-based solutions for resilient cities. Environ. Res. Lett. 16, 044008 https://doi.org/10.1088/1748-9326/abd9f4.

Hutchins, M.G., Qu, Y., Baker, H., 2023. Woodland establishment reduces nutrient losses to waterbodies in urban catchments: a review of the evidence. Water Resour. Res. e2022WR032626 https://doi.org/10.1029/2022WR032626.

Imberger, S.J., Thompson, R.M., Grace, M.R., 2011. Urban catchment hydrology overwhelms reach scale effects of riparian vegetation on organic matter dynamics. Freshw. Biol. 56, 1370–1389. https://doi.org/10.1111/j.1365-2427.2011.02575.x.

Jarvie, H.P., Jürgens, M.D., Williams, R.J., Neal, C., Davies, J.J.L., Barrett, C., White, J., 2005. Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: the Hampshire Avon and Herefordshire Wye. J. Hydrol. 304, 51–74. https://doi.org/10.1016/j.jhydrol.2004.10.002.

Ji, N., Liu, Y., Wang, S., Wu, Z., Li, H., 2022. Buffering effect of suspended particulate matter on phosphorus cycling during transport from rivers to lakes. Water Res. 216, 118350 https://doi.org/10.1016/j.watres.2022.118350.

Kinouchi, T., Seino, A., Takase, T., 2012. In-stream phosphate removal by suspended sediments transported from volcanic catchments. J. Hydrol. 448, 129–138. https://doi.org/10.1016/j.jhydrol.2012.04.034.

Kowe, R., Skidmore, R.E., Whitton, B.A., Pinder, A.C., 1998. Modelling phytoplankton dynamics in the River Swale, an upland river in NE England. Sci. Total Environ. 210, 535–546. https://doi.org/10.1016/S0048-9697(98)00036-9.

Mack, L., Andersen, H.E., Beklioğlu, et al., 2019. The future depends on what we do today – projecting Europe's surface water quality into three different future scenarios. Sci. Total Environ. 668, 470–484. https://doi.org/10.1016/j.scitotenv.2019.02.251.

Magritsky, D.V., Vasilenko, A.N., Frolova, N.L., Shevchenko, A.I., 2023. Temporal and spatial patterns of changes in thermal regime of the rivers in the northeast of the Asian part of Russia. 1. Assessment of changes in the water temperature. Water Resour. 50 (2), 190–201. https://doi.org/10.1134/S0097807823020124.

Matej-Lukowicz, K., Wojciechowska, E., Nawrot, N., Dzierzbicka-Głowacka, L.A., 2020. Seasonal contributions of nutrients from small urban and agricultural watersheds in northern Poland. Peer J 8, 8381. https://doi.org/10.7717/peerj.8381.

McGrane, S.J., 2016. Impacts of urbanisation on hydrological and water quality dynamics, and urban water management: a review. Hydrol. Sci. J. 61, 2295–2311. https://doi.org/10.1080/02626667.2015.1128084.

Miller, J., Hutchins, M.G., 2019. Thames catchment hydrometric and water quality data 2013-17. NERC Environmental Information Data Centre. https://doi.org/10.5285/793874b5-48b0-4971-8172-1cf97c35230f.

Neal, C., Jarvie, H.P., Williams, R., Love, A., Neal, M., Wickham, H., Harman, S., Armstrong, L., 2010. Declines in phosphorus concentration in the upper river Thames (UK): links to sewage effluent cleanup and extended end-member mixing analysis. Sci. Total Environ. 408, 1315–1330. https://doi.org/10.1016/j.scitotenv.2009.10.055.

Parsaie, A., Haghiabi, A.H., 2017. Computational modeling of pollution transmission in rivers. Appl Water Sci 7, 1213–1222. https://doi.org/10.1007/s13201-015-0319-6.

Prentice, M.J., Hamilton, D.P., Willis, A., O'Brien, K.R., Burford, M.A., 2019. Quantifying the role of organic phosphorus mineralisation on phytoplankton communities in a warm-monomictic lake. Inland Waters 9 (1), 10–24. https://doi.org/10.1080/20442041.2018.1538717.

Ryberg, K.R., Blomquist, J.D., Sprague, L.A., Sekellick, A.J., Keisman, J., 2018. Modeling drivers of phosphorus loads in Chesapeake Bay tributaries and inferences about long-term change. Sci. Total Environ. 616, 1423–1430. https://doi.org/10.1016/j.scitotenv.2017.10.173.

Suchowska-Kisielewicz, M., Nowogoński, I., 2021. Influence of storms on the emission of pollutants from sewage into waters. Sci. Rep. 11, 1–14. https://doi.org/10.1038/s41598-021-97536-5.

Timis, E.C., Hutchins, M.G., Cristea, V.M., 2022. Advancing understanding of in-river phosphorus dynamics using an advection-dispersion model (ADModel-P). J. Hydrol. 612, 128173 https://doi.org/10.1016/j.jhydrol.2022.128173.

Wade, A.J., Palmer-Felgate, E.J., Halliday, S.J., et al., 2012. Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring. Hydrol. Earth Sys. Sci. 16, 4323–4342. https://doi.org/10.5194/hess-16-4323-2012.

Walsh, C.J., Fletcher, T.D., Ladson, A.R., 2005. Stream restoration in urban catchments through redesigning stormwater systems: looking to the catchment to save the stream. J. North Am. Benthol. Soc. 24, 690–705. https://doi.org/10.1080/02626667.2015.1128084.

Wong, W.H., Dudula, J.J., Beaudoin, T., Groff, K., Kimball, W., Swigor, J., 2018. Declining ambient water phosphorus concentrations in Massachusetts' rivers from 1999 to 2013: environmental protection works. Water Res. 139, 108–117. https://doi.org/10.1016/j.watres.2018.03.053.

Xin, Z., Ye, L., Zhang, C., 2019. Application of export coefficient model and QUAL2K for water environmental management in a rural watershed. Sustainability 11, 6022. https://doi.org/10.3390/su11216022.

Zhang, W., Li, H., Xiao, Q., Li, X., 2021. Urban rivers are hotspots of riverine greenhouse gas (N_2O, CH_4, CO_2) emissions in the mixed-landscape Chaohu lake basin. Water Res. 189, 116624 https://doi.org/10.1016/j.watres.2020.116624.