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Research

Far-future hydrology will differentially change the phosphorus transfer continuum

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Abstract

Climate change is likely to exacerbate land to water phosphorus (P) transfers, causing a degradation of water quality in freshwater bodies in Northwestern Europe. Planning for mitigation measures requires an understanding of P loss processes under such conditions. This study assesses how climate induced changes to hydrology will likely influence the P transfer continuum in six contrasting river catchments using Irish national observatories as exemplars. Changes or stability of total P (TP) and total reactive P (TRP) transfer processes were estimated using far-future scenarios (RCP4.5 and RCP8.5) of modelled river discharge under climate change and observed links between hydrological regimes (baseflow and flashiness indices) and transfer processes (mobilisation and delivery indices). While there were no differences in P mobilisation between RCP4.5 and RCP8.5, both mobilisation and delivery were higher for TP. Comparing data from 2080 (2070–2099) with 2020 (2010–2039), suggests that P mobilisation is expected to be relatively stable for the different catchments. While P delivery is highest in hydrologically flashy catchments, the largest increases were in groundwater-fed catchments in RCP8.5 (+ 22% for TRP and + 24% for TP). The inter-annual variability of P delivery in the groundwater-fed catchments is also expected to increase. Since the magnitude of a P source may not fully define its mobility, and hydrological connections of mobilisation areas are expected to increase, we recommend identifying critical mobilisation areas to target future mitigation strategies. These are hydrologically connected areas where controls such as soil/bedrock chemistry, biological activity and hydrological processes are favourable for P mobilisation.

Keywords Mobilisation · Delivery · Impact · Water quality · Climate change · Critical Mobilisation Area

1 Introduction

Water quality and ecological status in European rivers is degraded by pollutant loss to waters [1]. Excessive phosphorus (P) from agricultural lands is a particular problem in freshwater systems as it enhances primary production and accelerates eutrophication [2]. Indeed, the intensity of agriculture is correlated with the ecological status of rivers across Europe [3]. Managing diffuse P loss in agricultural landscapes is a particularly pervasive challenge [4] and global change will likely increase nutrient and contaminant losses due to intensified hydro-meteorological drivers, higher nutrient inputs to meet growing food demand and sustained losses of nutrients from legacy stores in soils,

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sediments and aquifers [5]. The targeting of robust mitigation strategies will require an improved understanding of the underlying processes of nutrient loss that includes those occurring under changing climate conditions.

The P transfer continuum is a conceptual model linking P sources, transfers via mobilisation and delivery to a fresh water system and the resultant impacts [6] (Fig. 1). This model, which extended original thinking by Lemunyon and Gilbert [7] is widely used as a conceptual framework for the integrated assessment of river catchment P loss [8, 9]. The underlying hydrological processes of P mobilisation in land to water runoff are solubilisation or soil P detachment [10, 11]. Phosphorus delivery includes hydrological connection of P mobilisation areas via either surface runoff or subsurface pathways and P retention in the catchment landscape [10]. While P transfer processes are largely controlled by hydrological processes, P mobilisation is also influenced by chemical and biological factors, such as precipitation-dissolution, sorption–desorption, and microbial immobilization-mineralization [12].

A systematic and objective method for estimating and quantifying P transfers at catchment scale was introduced by Mellander et al. [13], which allowed for inter-catchment comparisons, assessment of inter-annual and intra-annual change/stability in catchments and identification of catchments' dominating P impact risk. The method uses ratios of high and low percentiles from long-term, high temporal resolution time-series data of P concentrations and mass loads. The empirical relation of the hydrological regime, expressed by indices of the catchment river baseflow and hydrological flashiness, was linked to P mobilisation and delivery indices using the terminology from the P transfer continuum, respectively. This suggests deduction of macro-scale catchment P transfer processes from river baseflow and hydrological flashiness, which are parameters that can be derived from hydrological models using weather parameters as input data. The main controlling factor for the baseflow is soil water transmissivity, the bedrock type and geological structure [14]. Topography and geomorphology also influence baseflow by affecting storage properties [15]. Land use also has a spatial influence on water recharge and baseflow [16]. Baseflow is typically low for rivers in catchments with impermeable soils and bedrock, and a flashy hydrology, and high in more permeable and groundwater-fed catchments [15]. We propose that the ability of a catchment to retain P due to high soil-geologic permeability factors will ultimately effect P mobilisation potential, particularly solubilisation. This will result in a wider range of stream P concentrations from low to high magnitude where the most permeable catchments will show the widest range. Hydrological flashiness is controlled by flood generating factors such as the frequency and magnitude of storm events [17], soil drainage [18] and tile drainage [19]. We propose that this energetic driver of P across and through the soil surface will be reflected in a large range of instantaneous P loads delivered to rivers where the largest range will be observed in the flashiest catchments. Weather parameters, such as rainfall, temperature and evapotranspiration, contribute to patterns in P concentrations in rivers [20] and together with land use are drivers for stability or changes in P transfer processes.

Addressing current and future problems with excess P losses to freshwaters requires climate smart mitigation measures and strategies that do not assume stationarity in our hydrological systems. This has been proposed in other work warning that mitigation methods to break the pathway of P in runoff (such as riparian buffer strips for example) may be overcome by changes in runoff patterns [21]. The next logical step is to gain further insights into the hydrological drivers of nutrient losses under future climate conditions of river discharge that model non-stationarity. Therefore, the objectives of this study were to: (i) use the empirical relation between P and hydrological indices to evaluate potential future changes in P transfer using discharge simulations representative of changing climate conditions, (ii) assess climate change influences on *P mobilisation* and *delivery* in six hydrologically contrasting agricultural river catchments, and (iii) estimate changes or stability of P *transfer* processes using projected scenarios of river discharge.
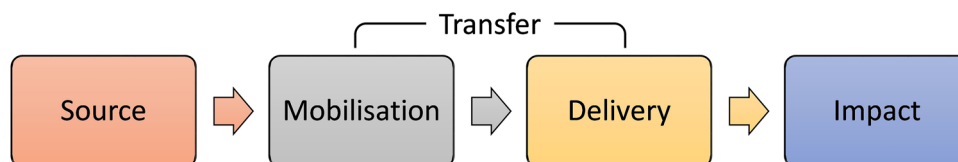
Fig. 1 The Phosphorus Transfer Continuum [6]. A conceptual model linking P sources, transfers via mobilisation and delivery to a fresh water system where it can have negative impacts

2 Materials and methods

2.1 Catchments

Three hydrological flashy catchments, with a relatively high *Flashiness Index (Q5/Q95)* [18] of 61–126, and three mostly groundwater-fed catchments, with a relatively high *Baseflow Index (BFI)* [22, 23] of 0.57–0.66, were used in the analysis (more details are provided in Sects. 2.2 and 2.3). The six study catchment observatories are monitored within the Irish Agricultural Catchments Programme [24] (Fig. 2) and were originally selected by a multi criteria analysis [25]. Selection criteria included catchments dominated by intensively managed agricultural land with high sources of nutrients, with different physical settings, no industrial and minimum domestic influences. The catchments were selected to be large enough (3.3 km^2–31 km^2) to include relevant hydrological and nutrient transfer processes, yet small enough to detect and build an understanding of these. The catchment scale is also small enough to engage with farmers and stakeholders and for being aware of any relevant changes in management.

2.1.1 Hydrologically flashy catchments

Ballycanew catchment is 11.9 km^2 with 77% of its area being used for mixed grassland. Three quarters of the catchment has poorly drained Gley soils and the remaining quarter has free draining Cambisols. The bedrock is rhyolite and slates. The annual average rainfall is 1037 mm and the annual average air temperature is 9.9 °C (2010–2020). The catchment has a flashy hydrology (*Q5/Q95* = 126) dominated by quick surface or near surface pathways [26]. The annual (2022) organic P source based on stocking rate was 20.3 kg org P ha^{-1}. *Corduff* catchment is 3.3 km^2 and located on a drumlin area dominated by mixed grassland (89%). On the hill tops the soils are Cambisols and on the slopes and valley bottoms there is a mix of stagnic Luvisols and Gleys. The bedrock is greywacke. The annual average rainfall is 1051 mm and the annual average air temperature is 8.8 °C (2010–2020).The hydrology is flashy (*Q5/Q95* = 111) and dominated by quick surface or near surface pathways. The annual (2022) organic P source based on stocking rate was 16.4 kg org P ha^{-1}. *Dunleer* catchment is 9.5 km^2 with a mix of grassland (44%) and arable land (34%). The soils are poorly drained Gleyic Luvisols (43%) and moderately drained Brown Earth soils (22%). The bedrock is calcareous greywacke and banded mudstone. The annual average rainfall is 869 mm and the annual average air temperature is 9.7 °C (2010–2020). The hydrology is slightly flashy (*Q5/Q95* = 61) but has also a relatively large contribution of groundwater (*BFI* = 0.66). The hydrological pathways

Fig. 2 Map of the location of six catchments monitored within the Agricultural Catchments Programme. Three catchments are hydrologically flashy (blue circle) and three are mostly groundwater-fed (green circle). The "Flashiness Index" (Q5/Q95) and Baseflow Index (BFI) is estimated for the period 2010–2020
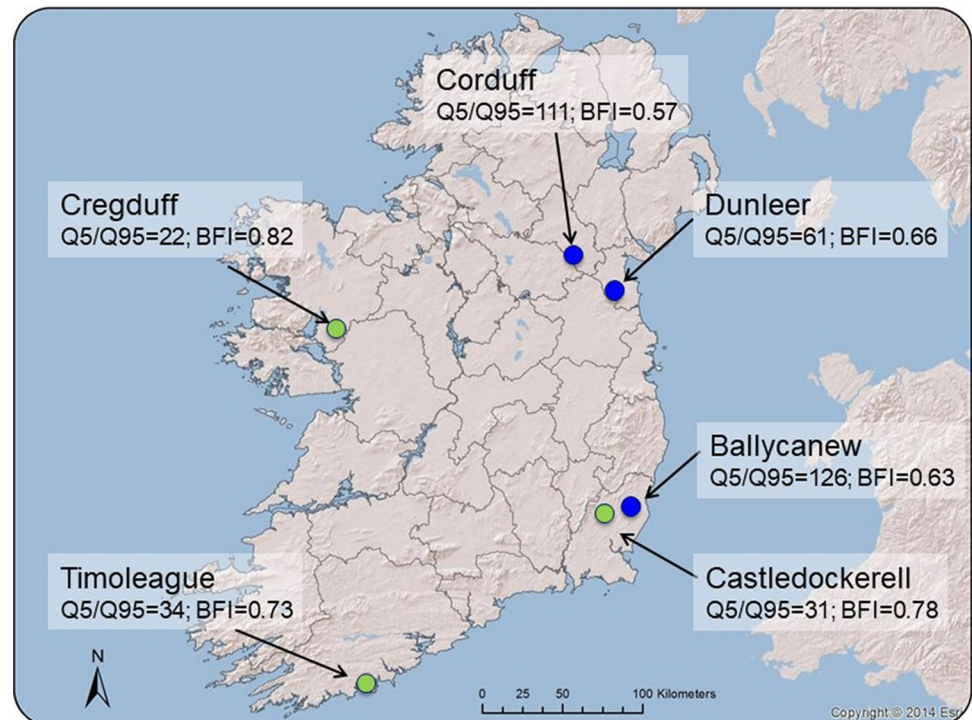
are a mix of quick, surface/near surface and subsurface [27]. The annual (2022) organic P source based on stocking rate was 14.6 kg org P ha^{-1}.

2.1.2 Groundwater-fed catchments

Timoleague catchment is 7.6 km^2 with 83% being grassland for dairy production. Most of the catchment (87%) has freely draining Cambisols. The bedrock is sandstones mixed with some mudstone and siltstone. The annual average rainfall is 1100 mm and the annual average air temperature is 10.2 °C (2010–2020). The catchment is largely groundwater-fed (*BFI* = 0.73) with dominating subsurface pathways [28]. The annual (2022) organic P source based on stocking rate was 23.7 kg org P ha^{-1}. *Castledockerell* catchment is 11.2 km^2 with 72% of its land being arable (72%). The soils are mostly freely draining Cambisols (80%). The catchment has a slate bedrock with a thick, permeable layer of weathered slate on top of the competent bedrock. The annual average rainfall is 1015 mm and the annual average air temperature is 10.0 °C (2010–2020). The catchment is largely groundwater-fed (*BFI* = 0.78) with dominating subsurface pathways [28]. The annual (2022) organic P source based on stocking rate was 9.8 kg org P ha^{-1}. *Cregduff* is a ca 31 km^2 karst spring contribution zone with almost its entire land being permanent grassland (92%). The soils are thin and freely draining Cambisols and Leptosols. The bedrock is pure limestone. The annual average rainfall is 1195 mm and the annual average air temperature is 10.0 °C (2010–2020). All hydrological pathways are subsurface, mostly in the fine and medium sized fissures of the limestone [29, 30]. The annual (2022) organic P source based on stocking rate was 14.4 kg org P ha^{-1}.

2.2 Monitored data

A stage-discharge curve was developed for each catchment using an Acoustic Doppler Current meter (OTT) and the velocity-area method. The river discharge was calculated from the stream water stage, which was monitored sub-hourly using an Orpheus Mini vented pressure instrument (OTT) installed in a stilling well adjacent to a flat-v weir of the catchments outlet.

Phosphorus concentrations were monitored sub-hourly in each catchment outlet using Hach Sigmatax-Phosphax P analysers [31, 32]. Concentrations of unfiltered total reactive P (TRP) and total P (TP) were monitored alternating the digestion step to provide sub-hourly TP and TRP data-points. The measurement range is 0.010 mg l^{-1}–5.000 mg l^{-1}.

Synchronous sub-hourly stream discharge and P concentration data were used for the period 1st Oct 2010 to 30th Oct 2020 to produce hourly and daily averages of concentrations and mass loads of TRP and TP.

2.3 Modelled data

A high spatial resolution ensemble (4 km) was derived by the Irish Centre for High End Computing (ICHEC) [33] and was used to examine changes in discharge across the six catchments. The data were derived by Murphy et al. [34] using an ensemble of dynamically downscaled climate change projections to force the SMART hydrological model (see below). The ensemble comprised five CMIP5 climate models (HadGEM2, EC-Earth, CNRM-CM5, MIROC5, MPI-ESM-LR) downscaled using COSMO-CLIM Version 5 [35]. Future discharge simulations were derived for two emissions scenarios. The Representative Concentration Pathway (RCP) 4.5 is a scenario where the radiative forcing is stabilised at 4.5 W m^{-2} in 2100 and represents a peak of global greenhouse gases emissions around 2040. The other scenario, RCP 8.5, stabilises radiative forcing at 8.5 W m^{-2} in 2100 and represents a fossil fuel intensive future with a continuing growth of greenhouse gas emissions and a 4.3 °C rise of the global average temperature by 2100.

The SMART model [36, 37] is a lumped-parameter hydrological model which has previously been used for both the assessment of the impact of climate change on water quality [38] and changes in catchments flow regimes [39]. The model was calibrated with 70% of the river discharge data from the six catchments using memetic algorithms with local search chains (MA-LS-Chains) [40] for optimisation. The remaining 30% of the data were used for validation. The Nash–Sutcliffe (NSE) and the logNSE objective functions [41] was used for an independent calibration of the model for both high and low flows. The median calibration scores were 0.72 for NSE and 0.58 for LogNSE. For the verification, the median scores were 0.72 (NSE) and 0.0.57 (LogNSE). In the same way as Murphy et al. [34], the modelled ensemble output data over the period 2010–2100 were used to represent three climatic periods 2020 (2010–2039), 2050 or near-future (2040–2069) and 2080 or far-future (2070–2099). The mean ensemble output data were used for comparisons of the two emission scenarios between the 2020s and 2080s.

Hydro Office BF + 3.0 [42] was used for estimating the *BFI* on daily monitored stream discharge over the period 2010–2020 and for the modelled discharge (2010–2100). The local minimum turning point method was used [43] choosing a five-day local minimum and a turning point factor of 0.9. The *Q5/Q95* is a hydrological flashiness metric based on the ratio of the 95th and 5th percentile of stream discharge. The 5th (low values, 95% exceeding), 50th (median) and 95th (high values, 5% exceeding) percentiles of daily stream discharge, P concentrations and mass loads over the period 2010–2020 and for the modelled discharge (2010–2100) were derived from Master Recession Curves created with Hydro Office FDC 2.1 [44].

2.4 Phosphorus transfer indices

The P transfer indices were calculated using sub-hourly concentrations of P and river discharge monitored in the catchments outlets (2010–2020). The P Mobilisation Index (*MI*) was derived from the ratio of the 95th and 5th hourly concentration percentiles of TRP and TP [13] and the P Delivery Index (*DI*) from the ratio of the 95th–50th and 50th–5th hourly mass load percentiles of TRP and TP [13]. The indices represent the whole catchment's propensity to transfer P. The *MI* represents the P mobilisation potential of solubilisation and soil detachment and the *DI* represents the hydrological delivery of P to the freshwater system. The P transfer indices are useful for identifying a catchment's dominating P impact risk and any changes or stability in this.

There is a positive and linear relationship between the long-term average *MI* and *BFI* and between the *DI* and Flashiness Index (*Q5/Q95)* in the six study catchments (Fig. 3 and Eqs. 1–2). The relationships were statistically significant (p < 0.05) for TRP *MI* and *BFI*, TRP *DI* and *Q5/Q95* and for TP *DI* and *Q5/Q95*, and a tendency to be significant for TP MI and BFI. The relationship of *MI* and *BFI* holds true for catchments where the hydrological regime dominates the influence of P mobilisation over the influence of chemistry and biological turnover. Catchments that largely retain P in the system will underestimate the *MI* and will be an outlier for the relationship of *MI* and *BFI*. This is the case for Cregduff, which has an intrinsic high P retention [29, 30] and was omitted from the *MI* and *BFI* relationship in Fig. 3.

Projected far-future scenarios of annual *MI* were derived for TRP and TP from the empirical relationships (Eqs. 1 and 2) to *BFI* (Fig. 3) as follows:
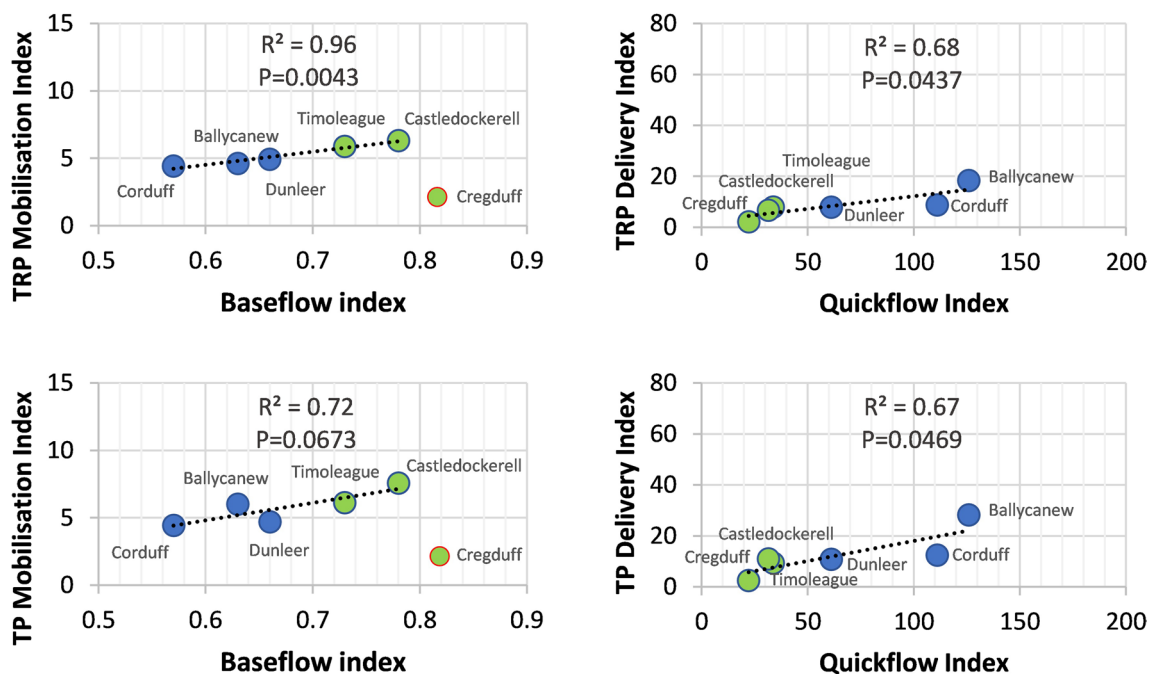
Fig. 3 The relationship between catchment P Mobilisation Index (MI) and Delivery Index (DI) with catchment hydrological characteristics comprising Baseflow Index (BFI) and Flashiness Index (Q5/Q95) for the six study catchments (blue = hydrologically flashy; green = groundwater-fed). Each symbol represents a catchment and was based on sub-hourly (2010–2020) data. Cregduff is as an outlier for MI due to high P retention (circle with red border) and was excluded from the MI and BFI relationship. From Mellander et al. [13]

$$TRP\ MI = 9.69 * BFI - 1.30 \tag{1}$$

$$TP\ MI = 12.97 * BFI - 2.97 \tag{2}$$

where the annual *BFI* was derived from the far-future projected river discharge scenarios. In a similar way, far-future scenarios of the annual *DI* were derived for TRP and TP from the empirical relationships (Eqs. 3 and 4) with *Q5/Q95* (Fig. 3):

$$TRP\ DI = 0.10 * Q5/Q95 + 2.25 \tag{3}$$

$$TP\ DI = 0.16 * Q5/Q95 + 2.24 \tag{4}$$

3 Results and discussion

3.1 Phosphorus mobilisation

While there were no differences in the mobilisation processes, as represented by the *MI*, between the RCP4.5 and RCP8.5 scenarios, there were small differences in *MI* between catchments of different hydrological character, and between mobilisation of TRP and TP (Fig. 4).

3.1.1 Influence of the flow regime

As expected, the catchments with a higher proportion of heavier clay soils had a relatively low baseflow (Corduff (*BFI* = 0.57), Ballycanew (*BFI* = 0.63) and Dunleer (*BFI* = 0.66)) and the catchments with mostly well-drained light soils had a relatively high baseflow (Timoleague (*BFI* = 0.73), Castledockerell (*BFI* = 0.78) and Cregduff (*BFI* = 0.82)) (Fig. 3). The estimation of *MI* based on catchment river baseflow relies on the linear relationship of catchment soil water infiltration/bedrock permeability and baseflow, as illustrated in Fig. 3. The difference in baseflow of the six catchments would therefore result from the difference in the flow regime, distribution of storage capacity (in both river channels and groundwater aquifers), and how the flow regime responds during recharge to changes in rainfall patterns and evapotranspiration [45]. There can also be a large influence on the spatial variability in baseflow generation caused by land use [16]. In the scenarios, the *MI*s were higher for TP, and the MI for both TP and TRP was higher in the groundwater-fed catchments (Fig. 4). The empirical relationship between *BFI* and *MI* (Fig. 3) illustrates that a higher *MI* is to be expected in groundwater-driven catchments, where soil infiltration is higher and P can more easily be mobilised via solubilisation than the hydrological flashy catchments with heavier soils and less vertical drainage or seepage. In catchments where particulate P is a large component of TP, it is likely that soil P detachment largely influences TP mobilisation, whereas P solubilisation mostly influences TRP mobilisation. Soil P detachment was likely more frequently occurring in surface pathways and solubilisation processes in belowground pathways, and so causing a higher *MI* for TP (including particulate P) in hydrologically flashy catchments and higher *MI* for TRP in groundwater-fed catchments.

Estimating the *MI* from *BFI* does not include the influence that warmer temperatures may have on mineralisation [46], fixation [47] or, in general, on soil biological turnover [48]. For example, not considering mineralisation could underestimate the *MI* in scenarios of a future warmer climate. The method also does not include the intrinsic catchment retention of P due to soil and bedrock chemistry. This is the case for the Cregduff spring contribution zone where P is readily retained by its Al- and Ca-dominated lithology [29], and explains why Cregduff is an outlier in the *MI* and *BFI* relationship (Fig. 3). This may be the case also for other karstic spring contribution zones where fine fissure flow dominates the pathways to the emerging spring. In Ireland, almost one fifth of the landscape is underlain by karst [50]. In such areas, the *MI* may be overestimated if the model is based on hydrology alone. In catchments where the soils and bedrock are high in Fe (such as in the Timoleague catchment) and/or acidic, the P may instead be more easily soluble and mobilised [28, 49]. Therefore, while the catchment hydrological characteristics provide good insight to the influence of hydrology on P transfer processes, the method can be improved by considering the dominant catchment soil and bedrock chemistry to refine mechanistic understanding.
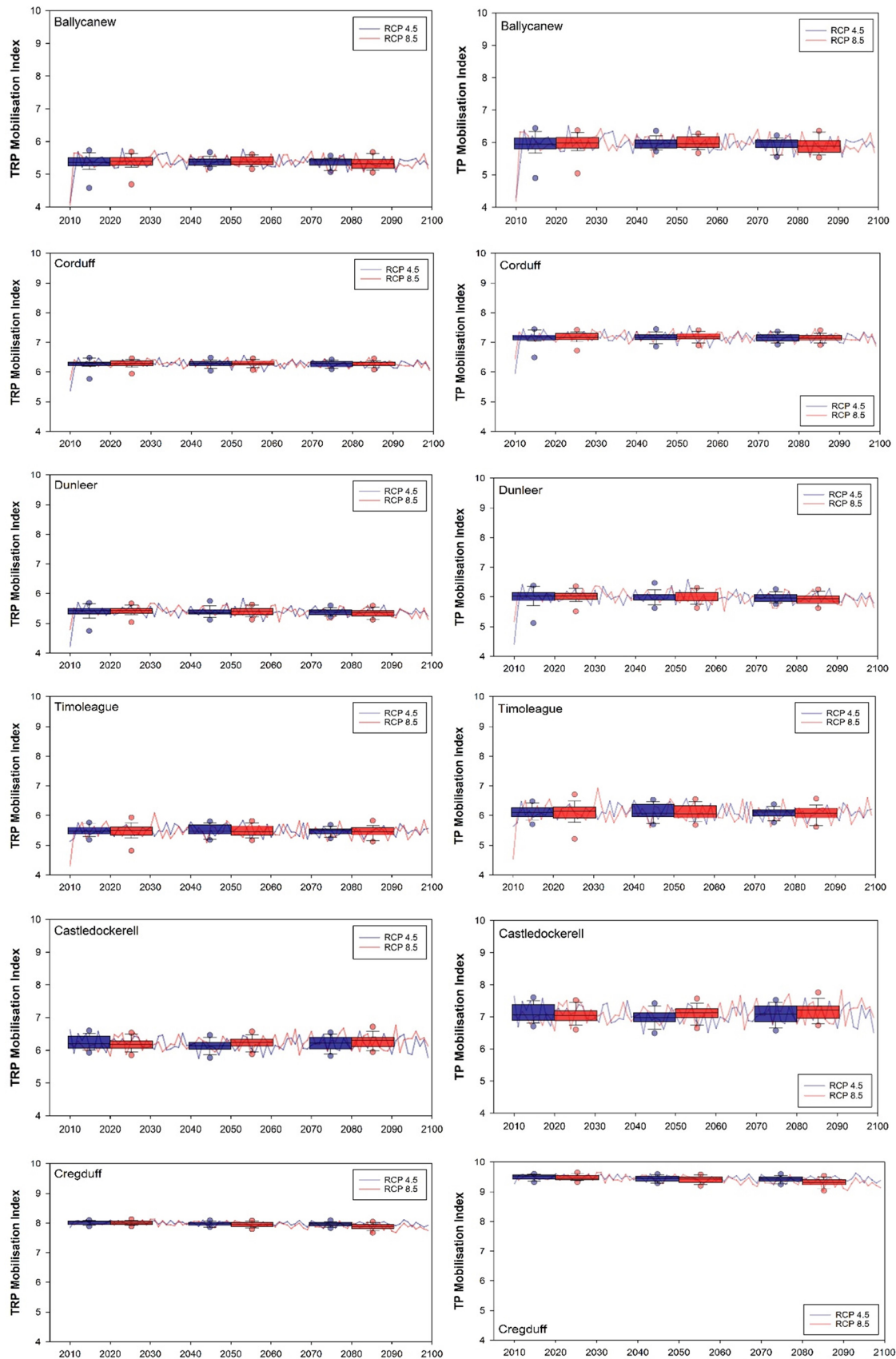
Fig. 4 Ensemble mean Mobilisation Index (MI) of TRP (left) and TP (right) for future climate scenarios (RCP4.5 and RCP8.5). Annual average MI (line) and 30-year average MI (box). The MI for Cregduff was estimated based on the relationship with hydrology and not considering the inherent P retention of that catchment

3.1.2 Mobilisation index far-future scenarios

Over the whole modelled period (2010–2100), the ensemble mean TRP *MI* was 13% higher, in both RCP4.5 and RCP8.5, for the three groundwater-fed catchments compared to the hydrologically flashy catchments. The TP *MI* was 15% higher in RCP8.5 and 16% higher in RCP4.5 for the three groundwater-fed catchments (Fig. 4). The ensemble mean TP *MI*, in both RCP4.5 and RCP8.5, was 11% higher in the hydrologically flashy catchments than the TRP *MI*. The ensemble mean TP MI, in both RCP4.5 and RCP8.5, was 13% higher than the TRP *MI* in the groundwater-fed catchments. For the *MI* estimated from the monitored data (2010–2020); it was 22% higher for TRP and 28% higher for TP in the groundwater-fed catchments compared to the hydrologically flashy catchments, when estimating *MI* based on hydrology alone and not taking the intrinsic P retention in the Cregduff spring contribution zone into account. Similar proportions, but not necessarily similar magnitudes, were expected since the far-future scenarios of *MI* were modelled using an empirical model of *BFI*.

Changes in *MI* were assessed based on the modelled ensemble mean of the three climatic periods 2020, 2050 and 2080. The mobilisation processes were relatively stable (− 2 to + 2%) in both scenarios (Fig. 5). The change in *MI* gradually decreased with decreasing *Q5/Q95* and increasing *BFI*. The hydrological processes that are proposed to influence changes in the *MI* did not change much in the modelled scenarios. It is, however, likely that the estimated *MI* in the scenarios were underestimated as climate change will influence other mobilisation processes, such as mineralisation and biological turnover, which was not included to the method used in this study that was based on the links to hydrology. There were, however, small increases in the hydrologically flashy catchments and decreases in the groundwater-fed catchments in RCP4.5 and decreases in all catchments except for Castledockerell in RCP8.5 where *MI* for both TP and TRP increase by the end of the century. In terms of both infiltration and surface/near surface runoff in the more intense RCP8.5 scenario, the arable-dominated groundwater-fed Castledockerell was likely more sensitive to changes in evapotranspiration, rainfall amounts and seasonality. In that catchment there is much seasonal variability in the presence of crops/bare soil and wetting of the freely draining soils. Weather, soil drainage and land use that promote infiltration and recharge of a catchment's storage will increase the baseflow. Other factors associated with higher evapotranspiration will reduce the baseflow. Changes in these factors may be linked to P mobilisation by P solubilisation (enhanced infiltration) and soil P detachment (enhanced saturation of bare soil with more erosive hydrological pathways on the surface). The latter is similar to that observed in that catchment, where the dominating well-drained soils were temporarily saturated in winter, causing extreme surface runoff driven P impact during large winter rain events [50]. Castledockerell was also a catchment with large changes in far-future modelled hydrology scenarios with, for example, the largest increase in high river flows (> 40%) and the largest inter-annual variability in flow [34]. Despite having a high baseflow (*BFI* = 0.78) this catchment is classified as a poorly productive aquifer with a relatively small storage capacity, which would make the catchment hydrologically sensitive to fluctuations in weather.

As a progression of the Critical Source Area (CSA) concept [51], which identifies hydrologically connected areas with a high soil P source, here we suggest the concept of Critical Mobilisation Areas (CMAs), *i.e.,* hydrologically connected

Fig. 5 Changes in MI between the modelled ensemble mean of the 30-year climatic periods 2020 (2010–2039) with 2080 (2070–2099) in the six study catchments with contrasting hydrology (Q5/Q95 = 22–126 and BFI 0.57–0.82)
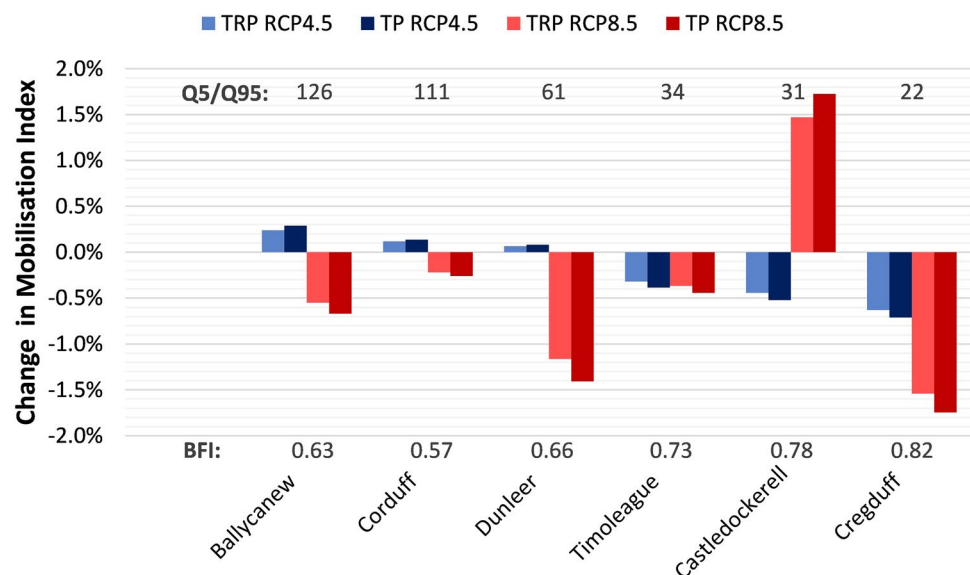
areas where controls such as soil/bedrock chemistry, biological activity and hydrological processes are favourable for P mobilisation. These could, for example, be areas with high infiltration rates, Fe-rich and/or acidic soils, and areas with shallow and fluctuating groundwater tables.

3.2 Phosphorus delivery

Unlike for P mobilisation, there were differences in P delivery between the RCP4.5 and RCP8.5 scenarios. There were also differences between catchments of different hydrological character, and between the delivery of TRP and TP (Fig. 6).

3.2.1 Influence of the flow regime

The *DIs* were derived from fluxes in P mass loads and were therefore more directly linked to the hydrology and hydrological processes than the *MI*. The catchments with a higher proportion of heavier clay soils had a high flashiness index (Ballycanew ($Q5/Q95 = 126$), Corduff ($Q5/Q95 = 111$), and Dunleer ($Q5/Q95 = 61$)) and the catchments with mostly well-drained light soils had a low flashiness index (Timoleague (($Q5/Q95 = 34$), Castledockerell ($Q5/Q95 = 31$) and Cregduff ($Q5/Q95 = 22$)) (Fig. 3). Here, the estimated *DI*, based on the catchments river flow flashiness, rely on the catchment flood generating factors. The difference in hydrological flashiness and *DI* between the six catchments would therefore result from the difference in runoff generating processes.

Hydrological connections of high *MI* areas within the catchment will determine P delivery, and the *DI* will increase with increased connectivity of mobilisation areas within the catchment. It is reasonable that such process are more pronounced in hydrologically flashy catchments with a larger proportion of surface transfer pathways due to poor soil drainage [26] and surface ditches or tile drainage [52]. With more frequent heavy rainfall events as expected by the climate scenarios, such pathways are likely to become more erosive [34] and deliver sediments and particulate P (included in TP). Delivery processes are therefore more responsive to climate changes in the two scenarios, and in particular in RCP8.5 and for the hydrologically flashy catchments.

3.2.2 Delivery index far-future scenarios

The TRP and TP *DI* successively increased over the three 30 year periods (2020, 2050 and 2080) in all six catchments and for both RCP4.5 and RCP8.5 (Fig. 7). While the *DI* was consistently higher in the hydrologically flashy catchments, the largest increase in *DI* from 2020 to 2080 was in the groundwater-fed catchments in RCP8.5, with a 22% increase for TRP and 24% increase for TP. This was only slightly higher than in the hydrologically flashy catchments where the increase was 21% and 23% for TRP and TP, respectively. Also in the RCP 4.5 scenario, there was a larger increase in *DI* by 2080 in the groundwater-fed catchments, where the increase was 16% and 19% for TRP and TP, respectively. In the hydrologically flashy catchments, that increase was 12% and 13%. An exception was the groundwater-driven catchment Castledockerell where the change in *DI* was lower for TP and in RCP8.5 (Fig. 7). Castledockerell is also the catchment where the MI was relatively high and the only catchment where the *MI* increased in RCP8.5. In that catchment and in Timoleague, the other groundwater-fed river catchment, there were large annual variabilities in TP *DI* (Fig. 7) but not for TRP *DI*.

The increase in the *DI* of all catchments can be explained by the increase in frequent rain events of higher magnitude, causing higher frequency of infiltration-excess runoff and increased connection of mobilisation areas. More frequent heavy rainfall can also lead to increased stream channel scouring [53]. The more intense RCP8.5 scenario predicts more heavy rainfall events and it is reasonable that *DI* will be higher for that scenario and for TP since large and erosive flow events can increase mobilisation by soil P detachment and will increase the subsequent delivery by connecting the mobilisation areas. In wet winters, even catchments with well-drained soils, such as Castledockerell, become saturated and temporarily hydrological flashy [50]. This explains the higher inter-annual variability estimated for the groundwater-fed catchments.

3.3 Considerations for mitigation strategies

The P transfer continuum (Fig. 1) [6] is a useful conceptual framework to understand catchment P impacts and the patterns that are possible due to climate change. If any of its components; *source*, *mobilisation* and *delivery*, are low or missing, there will be no or small impact. In the assessed catchments, the baseline mobilisation was already relatively high for the groundwater-fed catchments, and even predicted small changes would have the potential to influence the impact negatively in the
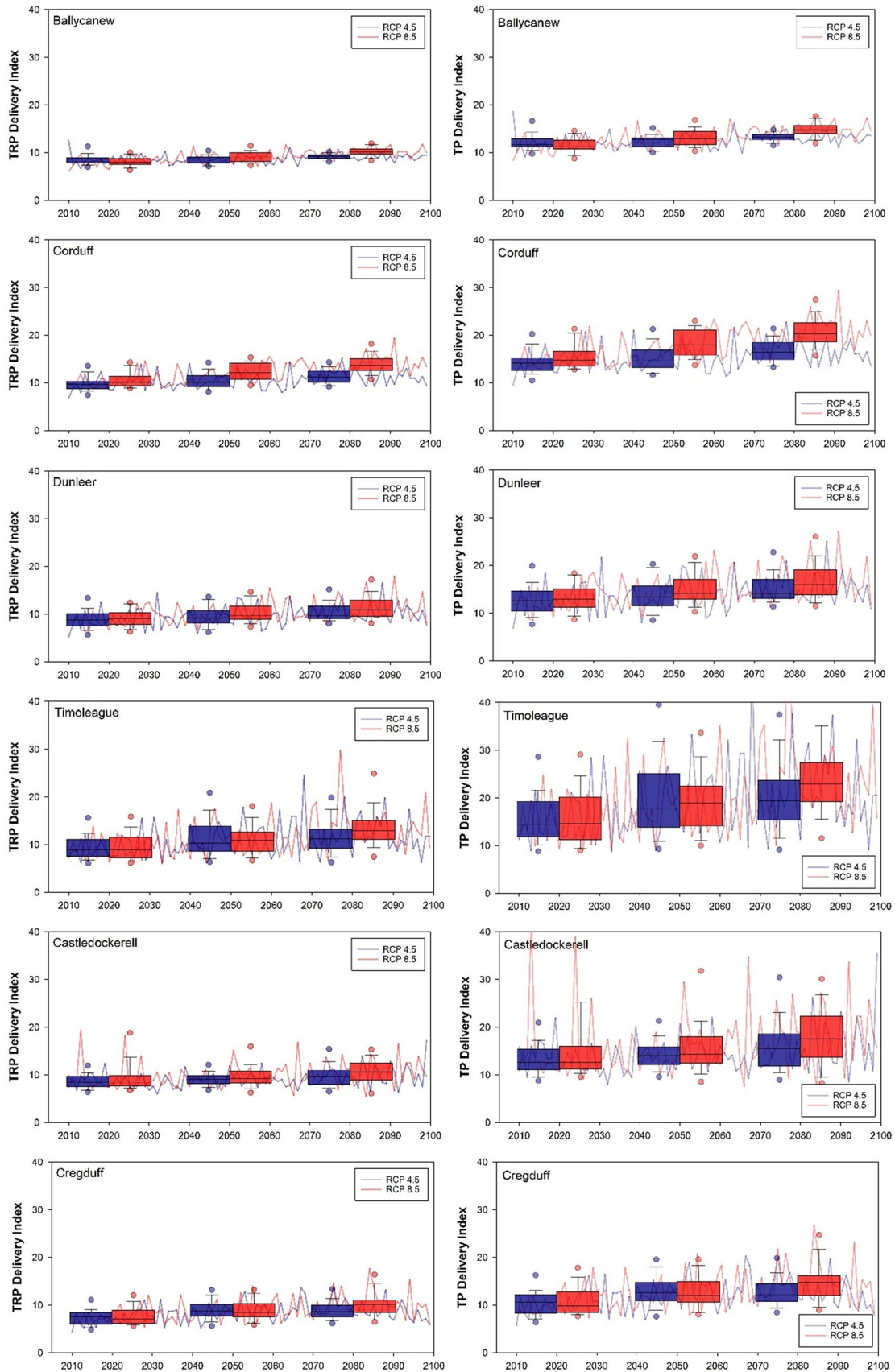
Fig. 6 Ensemble mean Delivery Index (DI) of TRP (left) and TP (right) for scenarios (RCP4.5 and RCP8.5). Annual average DI (line) and 30-year average MI (box)

Fig. 7 Changes in DI between the modelled ensemble mean of the 30-year climatic periods 2020 (2010–2039) with 2080 (2070–2099) in six catchments with contrasting hydrology (Q5/Q95 = 22–126 and BFI 0.57–0.82)
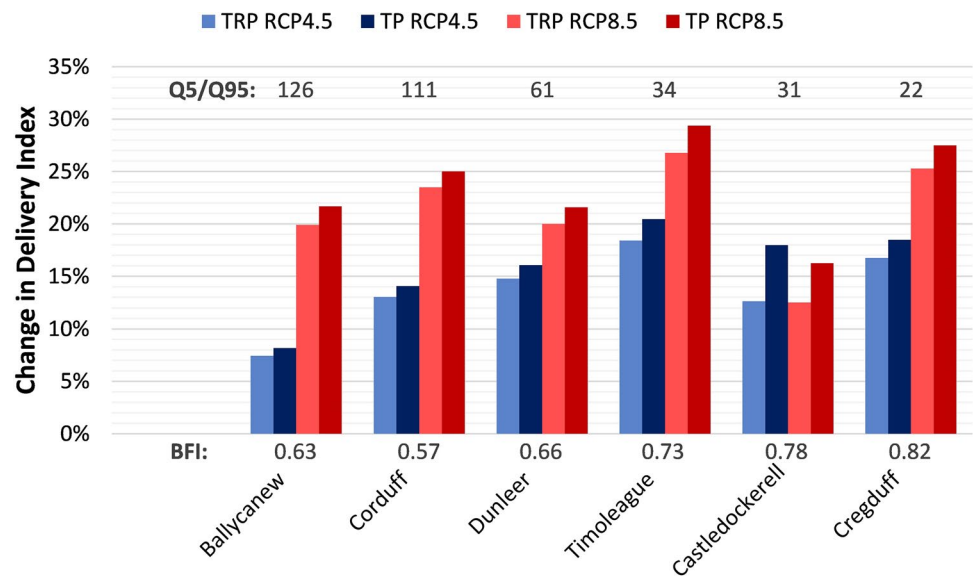
light of the predicted increase in *DI*. However, it is also important to consider legacy sources of P [4], which can be mobilised and cause an impact. In general, mobilisation processes were higher in groundwater-fed catchments and delivery processes higher in hydrologically flashy catchments. Some catchments may have a high intrinsic P retention that would largely reduce P mobilisation and, as such, also delivery and impact. Awareness of catchment chemistry and hydrology can help to identify the main risks for P loss in catchments [13] and the P impact of each catchment is unique and influenced by the frequency and magnitude of storm events, hydrological connectivity of mobilisation areas, soil chemistry, drainage status, and farming practices. While a P source can be high but not highly mobile, a P source can also be low yet highly mobile. Mitigation strategies would therefore benefit from the identification of CMAs, as a complement to CSAs. Less impact is to be expected in catchments with high intrinsic P retention, although it is unknown how these will respond to more frequent large storm events. Hydro-chemical models with subsurface delivery pathways and bio-geo-chemical process representation may provide more insight in such catchments.

The transfer indices are useful to identify a catchment's dominating transfer risk. For efficient and targeted mitigation strategies it is useful to identify CMAs, such as areas with high infiltration rates, Fe-rich and/or acidic soils, and areas with shallow and fluctuating groundwater tables, and where they overlap with CSAs. While this appears to be most useful for groundwater-fed catchments, P mobilisation in catchments with high P retention (Ca-dominated lithology and/or slow hydrological pathways) are unlikely to be P mobilisation risky. Since hydrological connectivity of mobilised P will increase, mitigation should focus on: (i) source management, such as implementing precision agriculture techniques (applying fertilisers in precise amounts and at specific times based on soil P levels and crop needs) [54], in both high mobilisation groundwater-fed catchments and in hydrologically flashy catchments; (ii) retaining P in the catchments by, for example, chemical soil amendments [48] or land use change, and; (iii) by intercepting delivery pathways. This could be by, for example, establishing buffer zones along water bodies and riparian areas to filter out excess P and sediment from runoff, stabilize soil and reduce erosion [55]. Buffer zones are advised to be site-specific and multi-functional, related to structural elements [56]. There is also potential for nature-based solutions, i.e. using natural features and processes in nutrient mitigation [57]. Future mitigation strategies need to consider combinations of more frequently occurring extreme weather events, changes in seasonality, and responses to these conditions in different catchment typologies. Furthermore, preparing landscapes for the conditions that are predicted to increase the flashiness index (and hence the *DI*), so that winter retained rainfall can offer both reduced peak flows and increased summer baseflow (hence lowering the flashiness index), can be undertaken more immediately via 'slowing the flow' measures [58]. Such considerations provide a basis for suggesting generic mitigation strategies which can be further tailored to local conditions.

4 Conclusions

Phosphorus can be mobilised from its source by solubilisation or detachment and delivered to catchment rivers via different hydrological pathways, where it may have a negative impact. Hydrological connectivity of mobilised P and retention along the pathways, will define its delivery. In water quality assessments of catchments, it is more common to have information about the sources and the monitored impact, whereas reliable insights to transfer processes are less common. Based on the simple relationship of P transfer processes to the hydrological regimes of catchments, scenarios of river flow under climate change in six hydrologically contrasting catchments were used to estimate P mobilisation and delivery processes for the coming century. Future scenarios (RCP4.5 and RCP8.5) of P transfer provide valuable information for more targeted future mitigation strategies to support adaptive management.

While there were no differences in the *MI* between RCP4.5 and RCP8.5, and P mobilisation was relatively stable throughout the century, there were differences in transfer between TP and TRP and between types of catchments. Both mobilisation and delivery was higher for TP and delivery processes were higher in the RCP8.5 scenario and in the groundwater-fed catchments. Both TP and TRP delivery is expected to increase in all catchments, in both RCP4.5 and RCP8.5, by the end of the century (more for TP and in RCP8.5). The risks for P loss is likely related to an increase in hydrological connectivity of mobilised P and/or reduction in P retention within the landscape, and inter-annual variability is expected to increase. Even if the *MI* is expected to be relatively stable, the mobilisation is, in general, high in most catchments and particularly in the groundwater-fed catchments. An increased connection of mobilisation areas would increase P delivery and therefore, the impact risk.

Insight to future P transfer processes and how these may vary in catchments of different character is highly valuable information for more resilient and targeted mitigation strategies. Since the magnitude of a P source does not define its mobility, and hydrological connections of mobilisation areas are expected to increase, we propose definition of Critical Mobilisation Areas (CMAs), *i.e.,* hydrologically connected areas where controls such as soil/bedrock chemistry, biological activity and hydrological processes are favourable for P solubilisation and soil P detachment.

Declarations

Competing interests The authors declare no competing interests.

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