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# Phosphorus mobilization and delivery estimated from long-term high frequency water quality and discharge data

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Efficient and targeted measures to mitigate nutrient losses to water are required to meet the challenges of increased food production and climate change. Diffuse pollution management requires insight into the underlying processes of nutrient transfer and its stability, but there are no standardized ways to evaluate phosphorus (P) mobilization and delivery at the catchments scale. Here we suggest a method that allows to systematically and objectively describe catchment scale processes of P transfer to water. Ten years of sub-hourly P concentration and hydrometric data from six agricultural catchments, with different physical characteristics, were assessed to introduce a method for estimation of a *P mobilization index* and a P *delivery index*. The former was defined as P detachment/solubilization expressed as ratios of P concentration percentiles, and the latter as connectivity/retention expressed as ratios of P mass load percentiles. Estimating these indices over several years provided insights on the stability of transfer processes over time and the identification of inter-annual trends. The *indices* were also used to quantify components of the P transfer continuum. This was used as a screening tool to compare and classify catchment specific and potential P loss risks. While the groundwater driven catchments had a higher *P mobilization index* for reactive P, the hydrologically flashy catchments had higher *delivery* indices for total P and particulate P + total organic P. Increasing or decreasing inter-annual trends were mostly found in catchments with a chemo-dynamic response in the discharge-concentration relationship. In three catchments the environmental quality standards were frequently exceeded caused by different risks and the P loss screening tool identified the type of risk. Development of the P *mobilization* and *delivery indices* was possible with long-term and high frequency monitoring of water quality and discharge from catchments of different typologies, together with a conceptual understanding of the catchments. More catchments of different typologies, management, scales and from different climatic zones are needed for further development of the indices.

KEYWORDS

**nutrients, transfer continuum, agriculture, risk model, percentiles, Q5/Q95, index**

## Introduction

Exessive phosphorus (P) and nitrogen (N) can be mobilized from agricultural landscapes and be delivered into rivers, lakes, estuaries, and coastal waters causing a negative impact on water quality and biodiversity (e.g., Carpenter et al., 1998; Schindler, 2006; Liu et al., 2021; Maúre et al., 2021). National and international legislation provides mitigation measures and targets. For example, as part of the Water Framework Directive (WFD) (2000/60/EC), the European Union (EU) requires all Member States to protect and improve water quality in all waters to achieve good ecological status by 2027. However, with an increasing population, more agrochemicals will likely be used to produce more food to ensure food security. To meet those requirements, and at the same time achieve WFD goals, efficient and targeted measures to mitigate nutrient losses are required (e.g., Schoumans et al., 2014; Vinten et al., 2017). Another challenge is the pressure caused by climate change with its inherent weather extremes that influences N and P loss differently across different catchments typologies (Mellander et al., 2018) and this requires additional mitigation measures (Ockenden et al., 2017). Knowledge and understanding of the dominating risks and the underlying processes for nutrient loss in the landscape, and when and where these mostly occur, will provide valuable information for such mitigation strategies.

Phosphorus is a particular problem in freshwater systems and the *P transfer continuum* was introduced as a conceptual model linking P from its source, *via mobilization* and *delivery*, to *impact* (Haygarth et al., 2005) and is a useful tool for assessing the integrated river catchment P loss risks. Phosphorus *mobilization* in land runoff was described as detachment or solubilization of soil P, and P *delivery* as transport including connection and retention in the landscape (Withers and Haygarth, 2007). The model has been widely used as a conceptual framework for integrated catchments studies such as the Irish Agricultural Catchments Programme (Fealy et al., 2010; Mellander et al., 2022) and the DEFRA Demonstration Test Catchments in the UK (e.g., McGonigle et al., 2014). Such studies require a consideration of the complexity and influence of the landscape, land management, and the sequence of hydrological events on both the transport and the balance between particulate and dissolved P (Beven et al., 2005). Diffuse pollution management would benefit from a standardized, systematic and objective method for evaluating P transfer at the catchment scale. This would allow to: (i) identify dominating risks for P loss, (ii) assess inter-catchments comparison, (iii) assess inter-annual variability/stability, and (iv) improve interpretations of output from water quality models assessing the influence of future climate and land use scenarios. However, such a method has not yet been published and the aim of the present study was to address this knowledge gap by quantifying the P transfer continuum.

High-frequency water quality data have quickly advanced our understanding of water quality processes (Rode et al., 2016) and facilitated, for example, more detailed contextualizations of the P transfer continuum (e.g., Bowes et al., 2005; Jarvie et al., 2011; Mellander et al., 2012; Bieroza et al., 2020). Long-term datasets of high frequency water quality parameters have further created new possibilities to systematically explore and describe catchment scale processes of P delivery to water. In a similar way to hydrologists using ratios of flow percentiles (PCTLs) to describe river flow "flashiness" (e.g., Gannon et al., 2022), or economists using income PCTLs to assess economic inequality (e.g., Smeeding, 2005), we hypothesize that ratios of P concentration PCTLs and mass load PCTLs can be useful to describe P transfer in a catchment. Since the ratio of high (95$^{th}$ PCTL) and low (5th PCTL) P concentrations is a measure of a catchment's range of concentrations it can be used to describe the integrated processes that mobilize P from its source to contribute to that concentration, such as soil P detachment and solubilization (Gburek et al., 2005). In a similar way, the ratio of high and low P mass loads reflects a catchments range of mass loads and integrates the processes that influence that delivery, such as hydrological connection and P retention (Preiner et al., 2020). The first objective of this study was to find a systematic and objective method to estimate catchment scale P transfer. Ten years of high frequency water quality and hydrometric data, from six small river catchments of different physical characteristics, was used to introduce a new method to describe catchment scale *P mobilization* and *delivery.* The second objective was to test the introduced method for an inter-catchment and inter-annual comparison of P transfer to provide insights to its stability or variability. The third objective was to use the indices together with the P transfer continuum as a screening tool to classify catchment specific and potential P loss risks. The different steps of the procedure are summarized in Figure 1.

## Materials and methods

### Sites description

Five river catchments and one karst spring contribution zone monitored within the Irish Agricultural Catchments Programme were assessed (here all termed catchments). The study catchments are located across Ireland (Figure 2) and are all dominated by intensively managed agricultural land (grassland or arable land), have different physical settings and have no industrial and minimum domestic influence. The catchments range in size from 3 to 32 km$^2$ (Table 1).

*Corduff* (3.3 km$^2$) is located in a drumlin area of Co. Monaghan in northeast Ireland. The catchment is dominated by mixed grassland (89%). Cambisols dominate the hill tops and stagnic Luvisols and Gleys on the hill slopes, foot slopes and

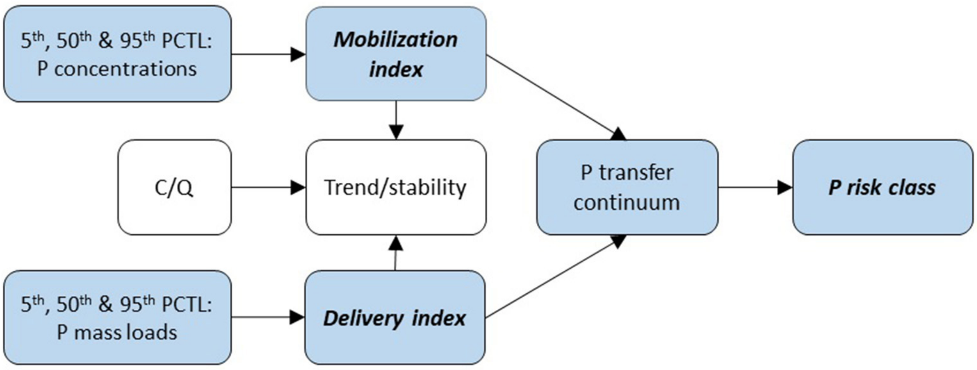


FIGURE 1
Flowchart of the steps included in a new proposed method for assessing diffuse P pollution at the catchment scale.

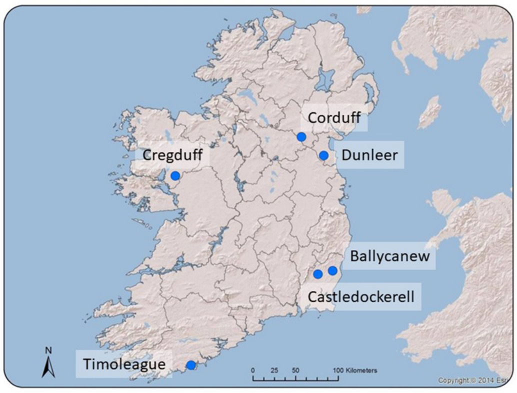


FIGURE 2
Location of the six study catchments within the Irish Agricultural Catchments Programme.

valley bottoms. The hydrological pathways are mostly quick and on the surface/near surface. The underlying geology is mainly greywacke. The average organic P source based on stocking rate was 20.8 kg org P ha$^{-1}$.

*Ballycanew* (11.9 km$^2$) is located in Co. Wexford in southeast Ireland. The catchment is dominated by mixed grassland (77%). Most of the soils are poorly drained (74% Gley soils) and the hydrological pathways mostly quick and on the surface/near surface (Mellander et al., 2015). The geology consists of rhyolitic volcanic and slates. The higher grounds have freely drained soil (26% Cambisols) and arable land for spring barley. The average organic P source based on stocking rate was 12.5 kg org P ha$^{-1}$. This period experienced agronomic intensification, with the amount of land under derogation increasing from 13% to 30% (under the E.U. Nitrates Directive, "derogation" is defined as an allowance to farm at livestock densities above the normal limit of 170 kg N ha$^{-1}$).

*Dunleer* (9.5 km$^2$) is located Co. Louth in northeast Ireland. The catchment consists of 34% arable and 44% grassland. About one-third of the soils are moderately to poorly drained (43% Gleyic Luvisols, 22% Brown Earth) and the hydrological pathways are mostly quick and on the surface/near surface (Mellander et al., 2012). The underlying geology consist of Ordovician-Silurian calcareous greywacke and banded mudstone. The average organic P source based on stocking rate was 10.6 kg org P ha$^{-1}$.

*Timoleague* (7.6 km$^2$) is located in Co. Cork in southwest Ireland. The catchment is dominated by permanent grassland for dairy production (83%). The soils are mostly freely draining (87% Cambisols). The geology is Devonian fine to medium grained sandstones with minor siltstone and mudstone and the hydrological pathways are mostly below-ground (Mellander et al., 2016). The average organic P source based on stocking rate was 18.1 kg org P ha$^{-1}$. This period saw agronomic intensification, with the percentage of land under derogation increasing from 50 to 66%.

*Castledockerell* (11.2 km$^2$) is located in Co. Wexford in southeast Ireland. Most of the catchment is arable (72%), mainly spring barley, winter barley, winter wheat and some oilseed rape. The soils are mostly freely draining (80% Cambisols). The bedrock formations consist of siltstones and slates. The slate has a highly weathered and permeable layer on top of the competent bedrock. The hydrological pathways are mostly below-ground (Mellander et al., 2016). The average organic P source based on stocking rate was 7.5 kg org P ha$^{-1}$.

*Cregduff* (ca 31.2 km$^2$) is a karst spring contribution zone in Co. Mayo, western Ireland. Most of the catchment is permanent grassland for sheep and beef (92%). The soils are relatively thin and dominated by freely draining Cambisols and Leptosols. The geology consists of a medium to thick bedded pure Carboniferous calcarenite (calcareous sedimentary rock) limestone. The topography is gently undulating and characterized by numerous karst features. The hydrological

TABLE 1 Description of the six study catchments.

| Catchment | Size [km$^2$] | Dominating land use | Dominating soil drainage class | Stocking rate** [kg org P/ha] | Rain* [mm/yr] | Discharge* [mm/yr] | Q5/Q95* | BFi* |
|---|---|---|---|---|---|---|---|---|
| Corduff | 3 | Grass | Poor | 20.8 | 1051 | 559 | 111 | 0.57 |
| Ballycanew | 12 | Grass | Poor | 12.5 | 1037 | 506 | 126 | 0.63 |
| Dunleer | 10 | Arable/Grass | Moderate | 10.6 | 869 | 419 | 61 | 0.66 |
| Timoleague | 8 | Grass | Well | 18.1 | 1100 | 679 | 34 | 0.73 |
| Castle dockerell | 11 | Arable | Well | 7.5 | 1015 | 528 | 31 | 0.78 |
| Cregduff | 31 | Grass | Well | 16.6 | 1195 | 170 | 22 | 0.82 |

*2010–2020, **2010–2018.

pathways are below-ground and mostly in the fine to medium fissures (Mellander et al., 2013). The average organic P source based on stocking rate was 16.6 kg org P ha$^{-1}$.

## Data collection

### Hydrometrics

Weather data were collected from a weather station (BWS200, Campbell Scientific, UK) located in the central lowlands within each catchment. These measured rainfall, air temperature, soil temperature, relative air humidity, solar radiation, wind speed, and wind direction on a 10-min basis.

In the river catchment outlet of each catchment a stage-discharge curve was developed (WISKI-SKED software, Germany) on a Corbett flat-v non-standard weir using the velocity-area method with an OTT Acoustic Doppler Current meter. The stream water level was recorded every 10 min with vented-pressure water level recorders (Orpheus Mini, OTT, Germany) installed in a stilling well close to the weir. Using the stage–discharge curve the stream discharge was calculated by converting the water level. In the Cregduff spring contribution zone the main spring discharge was calculated using an ultrasonic sensor (Thermo-Fisher time-of-flight area velocity meter) within an engineered uniform cross-section and these data were provided by the Irish Environmental Protection Agency.

### Phosphorus concentrations

Each catchment outlet was equipped with a bankside P analyser (Jordan et al., 2013). The bankside analyser uses Hach-Lange Sigmatax-Phosphax instruments that analyses unfiltered river water samples for total digested P (TP) and total molybdate-reactive P (TRP) concentrations sub-hourly. The measuring range is 0.010 mg l$^{-1}$ to 5.000 mg l$^{-1}$ and with a daily automated cleaning and calibration cycle. The combined particulate P and total organic P fraction (PP + TOP) was calculated by difference: TP – TRP.

### Phosphorus sources

The annual average organic P sources were estimated at the catchment scale based on annual stocking rates for the period 2010–2018 provided by the Department of Agriculture Food and the Marine. Other P sources that were not quantified were inorganic fertilizers and imported manures and slurries for recycling. These were considered to largely influence the total P source in the Dunleer and Ballycanew catchments. Phosphorus concentrations monitored in the catchment outlets can also be influenced by both agricultural and domestic point sources and both need consideration when linking water quality signals to diffuse agricultural sources.

## Analysis

### Phosphorus transfer indices and impact metric

Percentiles (5th, 50$^{th}$, and 95th) were calculated from hourly data of river discharge (Q), P concentrations and P mass loads for each hydrological year (1st October—30th September) over the period 2010–2020. The annual *P mobilization index* was calculated from the 5th and 95th percentiles of TP, TRP and PP + TOP concentrations according to Equation 1. And the annual *P delivery index* was derived from the 5th, 50$^{th}$, and 95th percentiles of TP, TRP and PP + TOP mass loads according to Equation 2.

$$\textbf{\textit{P mobilization index}} = \frac{\textbf{P conc 95th PCTL}}{\textbf{P conc 5th PCTL}} \tag{1}$$

$$\textbf{\textit{P delivery index}} = \frac{\textbf{P load 95th PCTL} - \textbf{P load 50th PCTL}}{\textbf{P load 50th PCTL} - \textbf{P load 5th PCTL}} \tag{2}$$

TABLE 2 Mann-Kendall trend categories after Connor et al. (2012).

| Trend category | S statistic | Confidence in trend |
|---|---|---|
| Increasing | > 0 | CF > 95% |
| Probably increasing | > 0 | 95% ≥ CF ≥ 90% |
| Stable | ≤ 0 | CF <90% and COV < 1 |
| Decreasing | < 0 | CF > 95% |
| Probably decreasing | < 0 | 95% ≥ CF ≥ 90% |
| No trend | > 0 | CF < 90% |
| No trend | ≤ 0 | CF <90% and COV ≥ 1 |

S, Statistic indicate the inter-annual concentration trend (positive, increasing; negative, decreasing), CF, Confidence Factor; COV, Coefficient of Variance.

The baseflow index (*BFi*) was calculated using Hydro Office BF+ 3.0 (Gregor, 2010) on daily Q over the period 2010–2020. The local minimum turning point method was used (Institute of Hydrology, 1980). While there is an empirical relationship between the number of days of local minimum and catchment area it was suggested that selecting a local minimum <5 days requires insight to the catchments recharge and response in groundwater level and it may be better to use a predefined value of 5 days (O'Brien et al., 2013). Based on this the default values of five-day local minimum and a turning point factor of 0.9 was used.

### Trends

A Mann-Kendall trend analysis was made for inter-annual trends of 5th, 50th, and 95th PCTLs of Q, P concentrations P mass loads, *P mobilization* and *P delivery* indices for the period 2010–2020. This was made using a Macro in MS Excel (GSI Mann-Kendall toolkit, Aziz et al., 2003; Connor et al., 2012). In this toolkit trends were categorized into *Increasing*, *Probably increasing*, *No trend*, *Stable*, *Probably decreasing* and *Decreasing* (Table 2).

# Results

## Percentiles of stream flow, phosphorus concentrations, and mass loads

Hydrological flashiness was highly affected by the drainage of the dominant soil types (Table 1). The catchments with a larger proportion of poorly drained soils; Ballycanew, Corduff and Dunleer, had the lowest *BFi* (0.63, 0.57, and 0.66 respectively) and the highest *Q5/Q95* (126, 111, and 61, respectively and which is the same expressed as *Q* $95^{th}$ *PCTL / Q* $5^{th}$ *PCTL*), and all with relatively high flows in the 95th PCTL (5.04, 5.55 and 3.67 mm /day respectively) and low flows in the 5th PCTL (0.04, 0.05 and 0.06 mm/day, respectively) (Table 3). The catchments with a large proportion of well-drained soils, Timoleague, Castledockerell and Cregduff, are largely groundwater driven with a high *BFi* (0.73, 0.78, and 0.82, respectively) and low *Q5/Q95* (34, 31, and 22, respectively). In Timoleague and Castledockerell the low flows (5th PCTL) were relatively high, 0.16 and 0.14 mm/day, respectively and the 50th PCTL 1.22 and 0.88 mm/day.

Three catchments; Timoleague, Ballycanew and Dunleer all had elevated 10-year median (50th PCTL) TRP concentrations (0.051, 0.064, and 0.096 mg/l, respectively) well above the environmental quality standard (EQS) of 0.035 mg TRP/l. The probability of exceeding the EQS was 80.7, 93.7, and 98.8%, respectively (Figure 3). While Dunleer had the highest concentrations of TP and TRP for both high and low PCTLs, Ballycanew had the highest concentration of PP + TOP in the high PCTLs. By contrast, in Cregduff, Castledockerell and Corduff catchments concentrations of P were relatively low. The median TRP concentration was below the EQS and the probability of exceeding EQS was 0.1, 22.5, and 29.0%, respectively (Figure 3). While Timoleague had the highest TP, TRP and PP + TOP mass loads in the low PCTLs, Ballycanew had the highest P loads in the high PCTL. Dunleer had high P mass loads in both high and low PCTLs (Table 3).

## Trends of streamflow, concentrations, and mass loads

Catchments of different flow and P export regimes revealed increasing and decreasing trends for the 5th, 50th, and 95th PCTLs of river flow, concentrations, and mass loads of P during the 10-year period (Table 3). The increasing trends were mostly observed in the Ballycanew catchment where there was an increasing trend of high flows (95th PCTL) and a likely increasing trend of median flows (50th PCTL). There was also an increase in low and average TP and TRP concentrations, low PP + TOP concentrations (5th PCTL) and a likely increase in the median PP + TOP concentrations. And there was an increase in the median TP and TRP mass loads and a likely increase in median PP + TOP, high TRP, and PP + TOP mass loads. In the Corduff catchment the occurrences of high TRP concentrations have increased and the high TP concentrations have likely increased. In Timoleague there were no changes in the flow over the period but there was an increase in the occurrence of high TP, TRP, median and high PP + TOP and a likely increase in median TP, low and median TRP concentrations. In that catchment there was only a likely increase in the high PP + TOP mass load. In Castledockerell catchment there were no observed trends in streamflow, however, there were counteracting trends in the concentrations and mass loads. While there was a decrease in low and median TRP concentrations and low TRP load, there was an increase in high PP + TOP concentrations and loads, a likely increase in high TP concentrations and load, and median PP + TOP concentrations. In Cregduff there was an

TABLE 3 The 5th, 50th, and 95th PCTL of river discharge, P concentrations and P mass loads for the six study catchments.

| | Percentile | Corduff | Ballycanew | Dunleer | Timoleague | Castledockerell | Cregduff |
|---|---|---|---|---|---|---|---|
| Q | 5th | 0.05 | 0.04 | 0.06 | 0.16→ | 0.14 | 0.05↑ |
| [mm/d] | 50th | 0.84 | 0.60↗ | 0.64→ | 1.22→ | 0.88 | 0.45 |
| | 95th | 5.55 | 5.04↑ | 3.67→ | 5.39 | 4.40 | 1.11 |
| TP | 5th | 0.025→ | 0.051↑ | 0.073↗ | 0.042↗ | 0.016→ | 0.016↓ |
| [mg/l] | 50th | 0.044 | 0.090↑ | 0.132 | 0.075↑ | 0.030→ | 0.021↘ |
| | 95th | 0.116↗ | 0.299 | 0.341 | 0.257 | 0.119↗ | 0.032→ |
| TRP | 5th | 0.014→ | 0.037↑ | 0.050→ | 0.027↗ | 0.010↓ | 0.011 |
| [mg/l] | 50th | 0.025 | 0.064↑ | 0.096 | 0.051↗ | 0.019↓ | 0.016 |
| | 95th | 0.062↑ | 0.171 | 0.246 | 0.159↑ | 0.063→ | 0.022→ |
| PP+TOP | 5th | 0.008 | 0.010↑ | 0.015→ | 0.012 | 0.004 | 0.002→ |
| [mg/l] | 50th | 0.016 | 0.022↗ | 0.030→ | 0.023↑ | 0.010↗ | 0.006↘ |
| | 95th | 0.065→ | 0.138→ | 0.124 | 0.104↑ | 0.052↑ | 0.013↘ |
| TP | 5th | 0.026 | 0.050 | 0.091→ | 0.118→ | 0.056→ | 0.010↗ |
| [g/d] | 50th | 0.320 | 0.445↑ | 0.736 | 0.852 | 0.226 | 0.089↗ |
| | 95th | 3.979→ | 11.595 | 7.668 | 7.749 | 2.091↗ | 0.281↗ |
| TRP | 5th | 0.017→ | 0.039 | 0.070→ | 0.075→ | 0.041↓ | 0.009 |
| [g/d] | 50th | 0.196 | 0.338↑ | 0.552 | 0.577 | 0.153 | 0.065↑ |
| | 95th | 1.775 | 5.843↗ | 4.362 | 4.544 | 0.904 | 0.184↑ |
| PP+TOP | 5th | 0.007→ | 0.010 | 0.017→ | 0.033→ | 0.012→ | 0.001 |
| [g/d] | 50th | 0.116 | 0.104↗ | 0.162 | 0.258 | 0.070 | 0.024→ |
| | 95th | 2.243→ | 5.407↗ | 3.170→ | 3.025↗ | 1.137↑ | 0.102→ |

The data is based on 10 years (1st October 2010 to 30th September 2020) of hourly data.
The colour indicate the Mann-Kendall inter-annual trend over the period (red ↑, increasing; orange ↗, probably increasing; light blue →, stable; dark green ↓, decreasing; light green ↘, probably decreasing).

increase in low flows and in median and high TRP loads, and a likely increase in low, median, and high TP load. In the same catchment there was a decrease in low TP concentrations and a likely decrease in median and high PP + TOP concentrations. In Dunleer many parameters were unchanged but there was a likely increase in low TP concentrations.

## Timing and duration of high concentrations and mass loads

For mitigation strategies it is often useful to know when high P concentrations and mass loads most frequently occur. The occurrence and duration of high (95th PCTL) P concentrations varied for different P fractions over the year, and between the catchments (Figure 4). The duration of high P concentrations was typically longer in the summer months in all of the study catchments, and mostly so in the hydrologically flashy catchments with lower baseflow. This seasonality was more pronounced for TRP. The duration of high TP and PP + TOP concentrations was more uniform throughout the year. In all the catchments, high concentrations of TRP occurred <5% of the time in the first 5 months of the year. During that time there were more often high TP and PP + TOP concentrations, but in Timoleague that difference was smaller. In October to December, the duration of high P concentration decreased in all catchments but was longer than in the beginning of the year. During that time there were more frequently high TP and PP + TOP concentrations. In Timoleague there were more frequent high TRP concentrations occurring in winter than in Castledockerell where there instead there were higher TP and PP + TOP concentrations occurring in both autumn and winter. In Cregduff a large part of May, and more so June, had high PP + TOP concentrations.

The duration of high mass load of P was typically longer in winter and autumn months in all catchments. For mass loads there was less variability between the different P fractions in all catchments and throughout the year than there was for concentrations. In most of the catchments the high P loads occurred more than 5% of each month in January to March and in October to December. This increased up to 16% of the time in January in Cregduff.

## Mobilization and delivery index

The catchments propensity to transfer P at the catchment scale were estimated by introducing the *mobilization* and

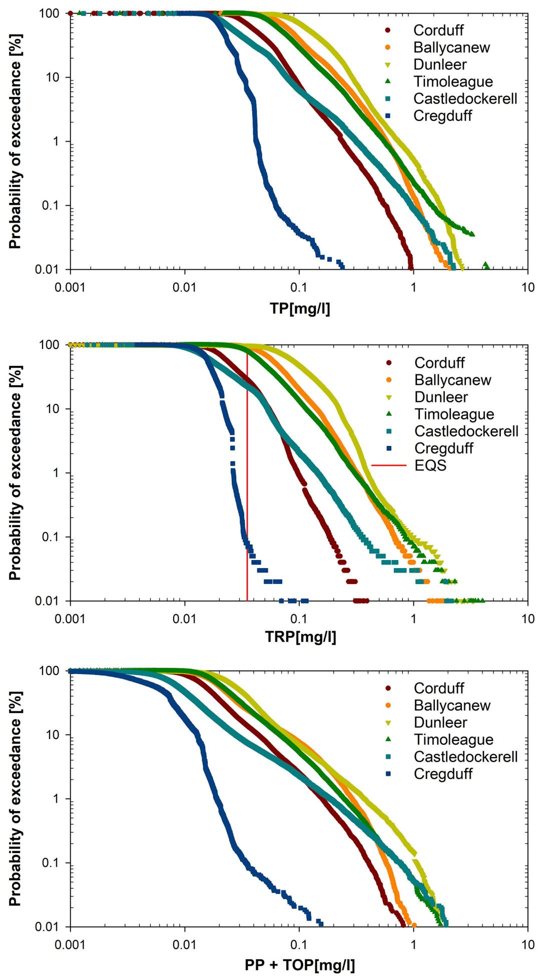


FIGURE 3
The probability of exceedance (percent time) for TP, TRP and PP + TOP concentrations in the six study catchments for ten hydrological years (1st October 2010 to 30th September 2020) based on hourly average concentrations. The Environmental Quality Standard (EQS) of 0.035 mg TRP/l is marked with a vertical red line.

*delivery indices for each year*. The average *mobilization indices* ranged from 2.0 to 7.6 for TP, from 2.0 to 6.7 for TRP, and from 8.1 to 17.5 for PP +TOP. The catchments in Figure 5A were ranked based on their *mobilization index*, which show distinct differences between sites. The higher indices for PP + TOP are in agreement with this fraction being the most mobile (e.g., Némery et al., 2005; Bilotta et al., 2008). Castledockerell catchment had the highest average *mobilization index* for all P fractions and had the largest inter-annual variability. The average *mobilization indices* were also relatively high in Timoleague for TP (6.1) and TRP (6.0). Ballycanew, a hydrologically flashy catchment with a large proportion of quick surface pathways, had a relatively high *mobilization index* of TP (6.0) and PP + TOP (12.6). However, with a low groundwater contribution there was a relatively low *mobilization index* for TRP (4.7). The 5th and 50th concentration PCTLs had increased for TP and PP + TOP, leading to a decrease in the *mobilization index* trend. Both Dunleer and the Corduff catchments had relatively low *mobilization indices* and with low inter-annual variability for all P fractions. Cregduff (a karst catchment) had the lowest average and lowest inter-annual variability of mobilization for TP (2.0) and TRP (2.0). However, there was a relatively high *mobilization index* (12.7) and large inter-annual variability of PP + TOP.

The *P delivery index* represents the range of P mass load, which reflects the integrated connection and transfer of P sources within the catchment. The average *delivery indices* ranged from 2.6 to 28.7 for TP, from 2.3 to 19.6 for TRP, and from 4.3 to 54.7 for PP +TOP (Figure 5B). Ballycanew catchment had the highest delivery of all P fractions. That was also the case for the *delivery indices*, which was more than double in Ballycanew compared to Castledockerell (TP = 28.7, TRP = 19.6 and PP + TOP = 54.7 compared to TP = 12.0, TRP = 7.3 and PP + TOP = 20.6). This is despite Castledockerell having higher *mobilization indices*. In Ballycanew there was a likely increase in the *delivery* of PP + TOP. Corduff and Dunleer catchments had relatively high *delivery indices* (TP = 12.9 and 11.3, TRP = 9.3 and 8.4, and PP + TOP = 20.2 and 21.4 respectively). In Dunleer the *delivery indices* for TP and TRP decreased. Similar to the *mobilization indices*, Cregduff (karst) catchment had the lowest average *delivery index* (TP = 2.6, TRP = 2.3 and PP + TOP = 2.4) and the lowest inter-annual variability.

## Catchment phosphorus export regime

The catchment P export regime was explored using the C-Q relation for the six study catchments. In Corduff and Timoleague all fractions of P appeared to be chemo-dynamic for the monitored flow range (Figure 6). In these catchments, both particulate and soluble P mobility and delivery were not limited, and concentrations increased with larger flow events. In Ballycanew, Dunleer, and Castledockerell TRP was chemo-static and the TP and PP + TOP was chemo-dynamic for the monitored flow range. In Cregduff only the PP + TOP was chemo-dynamic.

The increasing or decreasing trends observed in the mobilization and *delivery indices* (Figure 4) mostly coincided with the P fractions and catchments that were chemo-dynamic. In the catchments where there was an increasing trend in the *mobilization index* (for TP in Castledockerell and Corduff, for TRP in Corduff and for PP + TOP in Timoleague), there was also a chemo-dynamic response to the flow and an increase in the 95th PCTL concentration. In Ballycanew catchment there was a decreasing trend in the *mobilization index* for TP and PP + TOP, and there was a chemo-dynamic response to flow and an increasing trend in the *delivery index* of PP + TOP. In

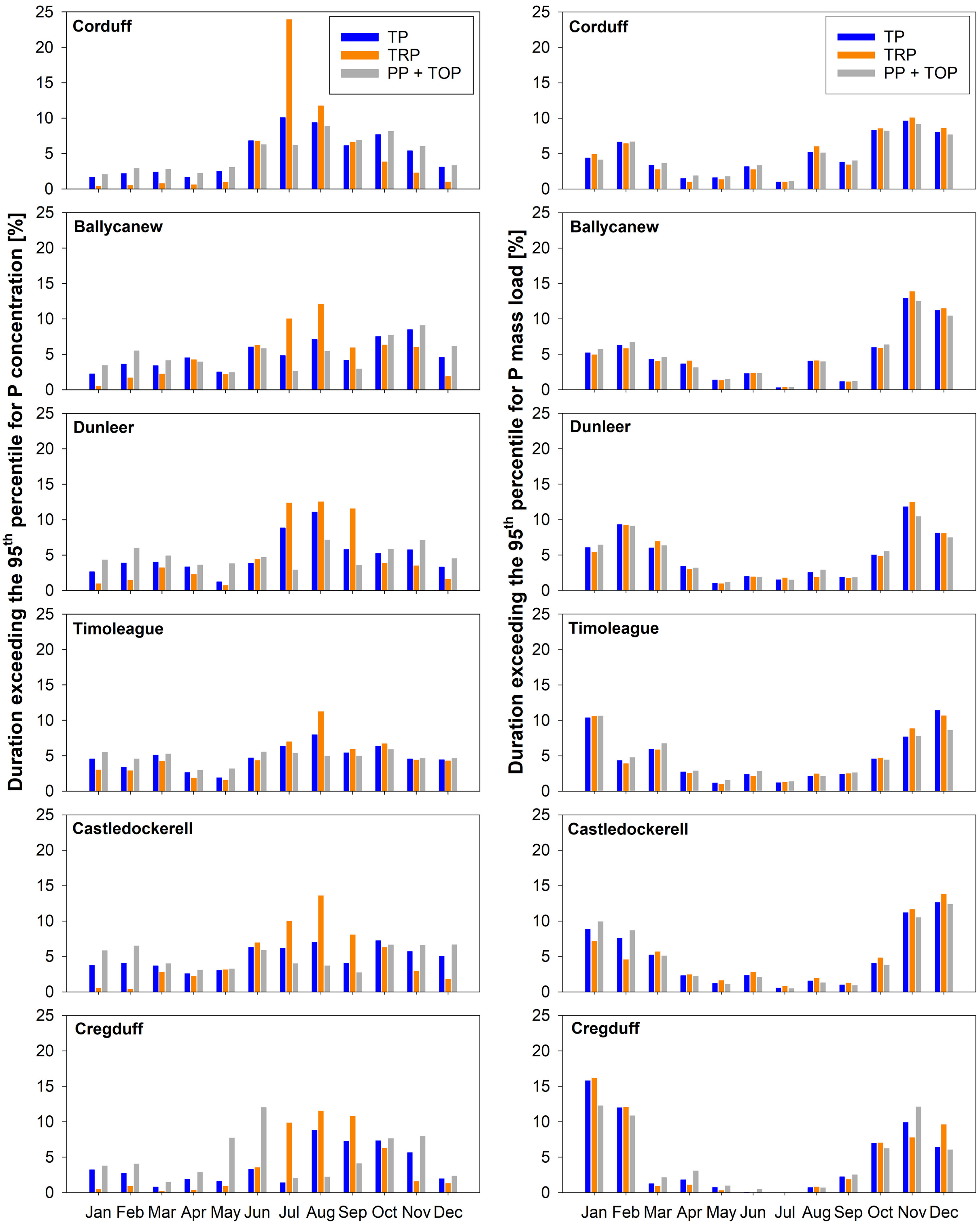


FIGURE 4
Duration of time per month (percent) exceeding the 95th PCTL of P concentrations (left) and P mass loads (right) for the six study catchments. The data is based on hourly averages of concentrations and hourly totals of mass loads for 10 years (1st October 2010 to 30th September 2020).

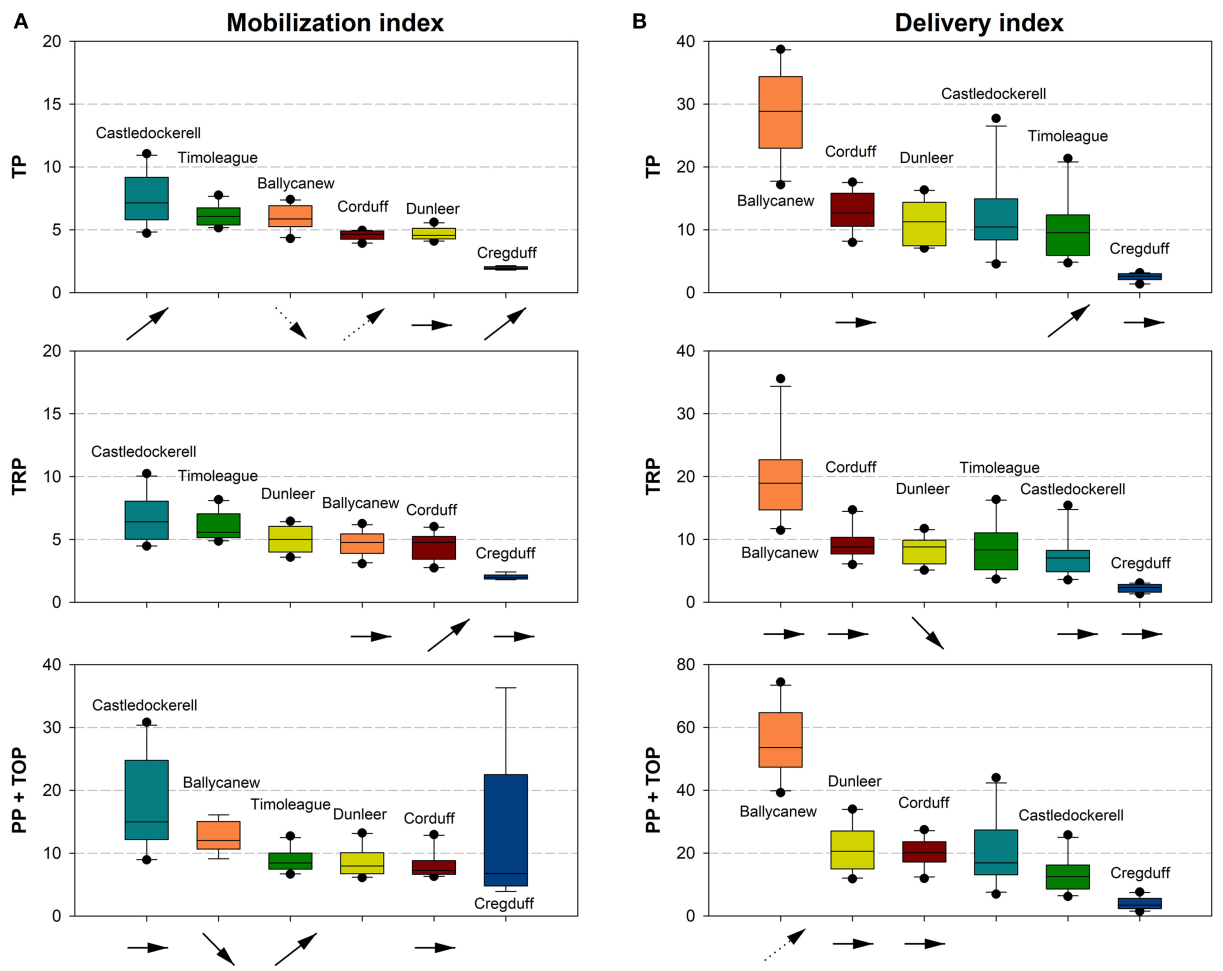


FIGURE 5
**(A)** *Mobilization indices* and **(B)** *Delivery indices* of TP, TRP, and PP + TOP in six agricultural catchments. The indices are based on sub-hourly averages of P concentrations and mass loads for ten hydrological years (1st Oct 2010 to 30th Sep 2020). The arrows indicate the Mann-Kendall inter-annual trends over the period (horizontal arrow, stable; whole upward arrow, increasing; dashed upward arrow, probably increasing; whole downward arrow, decreasing; dashed downward arrow, probably decreasing).

that catchment there was also an increase in the 50th and 95th PCTL flow, concentrations and mass loads. There was also a decreasing trend in the *delivery index* of TP in Dunleer, which was chemo-dynamic, and also in TRP which was chemo-static.

## Catchment scale P loss risk

A screening tool was developed to aide identification of the specific or potential catchment type of P loss risk. Following the P transfer continuum model, two of the six study catchments (Corduff and Timoleague) had relatively high P *sources* (above average of the six catchments) based on organic stocking rates alone (Figure 7). However, the size of organic stocking rate is likely to oversimplify the P source on a field basis. Another two catchments (Ballycanew and Dunleer) had relatively low P *sources* based on livestock, but are both considered as high *source* catchments since in these two catchments organic manures are known to be added.

Three catchments (Ballycanew, Dunleer, and Timoleague) had a high P *impact* with 10-year average TRP concentrations exceeding the EQS (Figure 7). Ballycanew catchment was *mobilization* and *delivery* risky for TP and PP + TOP and *delivery* risky for TRP. In Dunleer there was a high TP and PP + TOP *impact* despite relatively low *mobilization* and *delivery indices*. While Timoleague catchment was TP and TRP *mobilization* risky, it was not PP + TOP *mobilization* risky. Cregduff catchment was not P risky for any of the fractions, however this site did have high *mobilization* of PP + TOP which was not reflected in the *impact*.

Corduff catchment had a high *source* of P but a low *impact*, since the P was not highly *mobilized* or *delivered*. There was

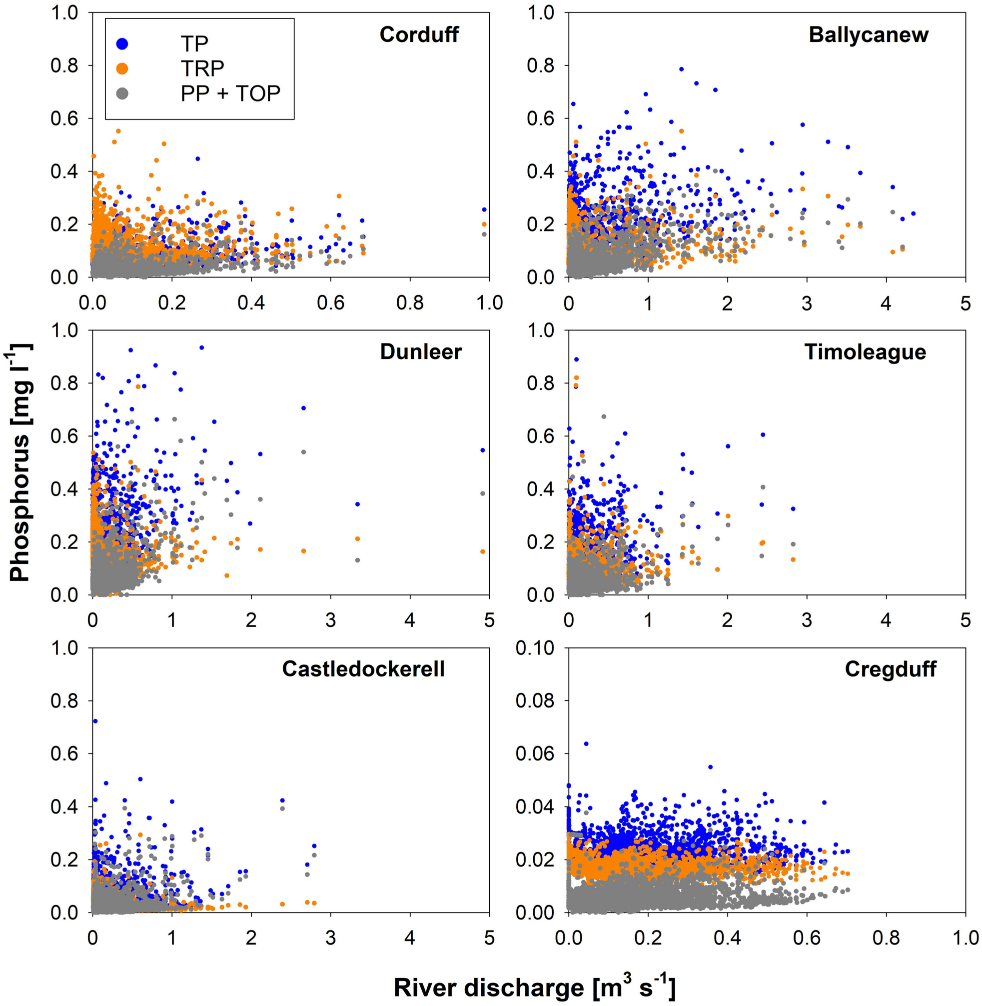


FIGURE 6
Daily average river discharge and concentrations of TP, TRP and PP + TOP for 10 years (1st October 2010 to 30th September 2020) in the six study catchments.

already an increasing trend in the TRP *mobilization index* (Figure 5A). Cregduff could also become a high *impact* TP and TRP loss risky catchment with an increased *mobilization* and/or *delivery index*. The catchment is further susceptible to changes in TP and PP + TOP due to its chemo-dynamic nature (Figure 6). Castledockerell potentially a *mobilization* risky catchment for all fractions of P, but had relatively low P *sources* and low *impact*.

# Discussion

## Stream flow and phosphorus loss to water

Hydrological flashiness was well-reflected by the dominating soil drainage in each catchment. The three catchments with mostly poorly drained Gleysol soils (Ballycanew, Corduff, and Dunleer) had the flashiest hydrology (Table 1), with a large component of quick surface pathways (Mellander et al., 2012). The catchments with a larger proportion of well-drained Cambisol soils (Timoleague, Castledockerell, and Cregduff) had lower hydrological flashiness, higher baseflow (Table 1), and were dominated by slow below-ground pathways (Mellander et al., 2013, 2016). Such catchments typically have relatively high flows in the lower PCTLs (Donnelly et al., 2016), which was also the case for Timoleague and Castledockerell. While the hydrology largely influenced the mass loads of all P fractions, there are also other factors such as *source* pressure (Kusmer et al., 2019), land use (Arheimer and Lidén, 2000) and biogeochemical processes (Turner and Haygarth, 2001) that affect the *mobilization* and *delivery* influencing the P concentrations and mass loads in the streams. Timoleague

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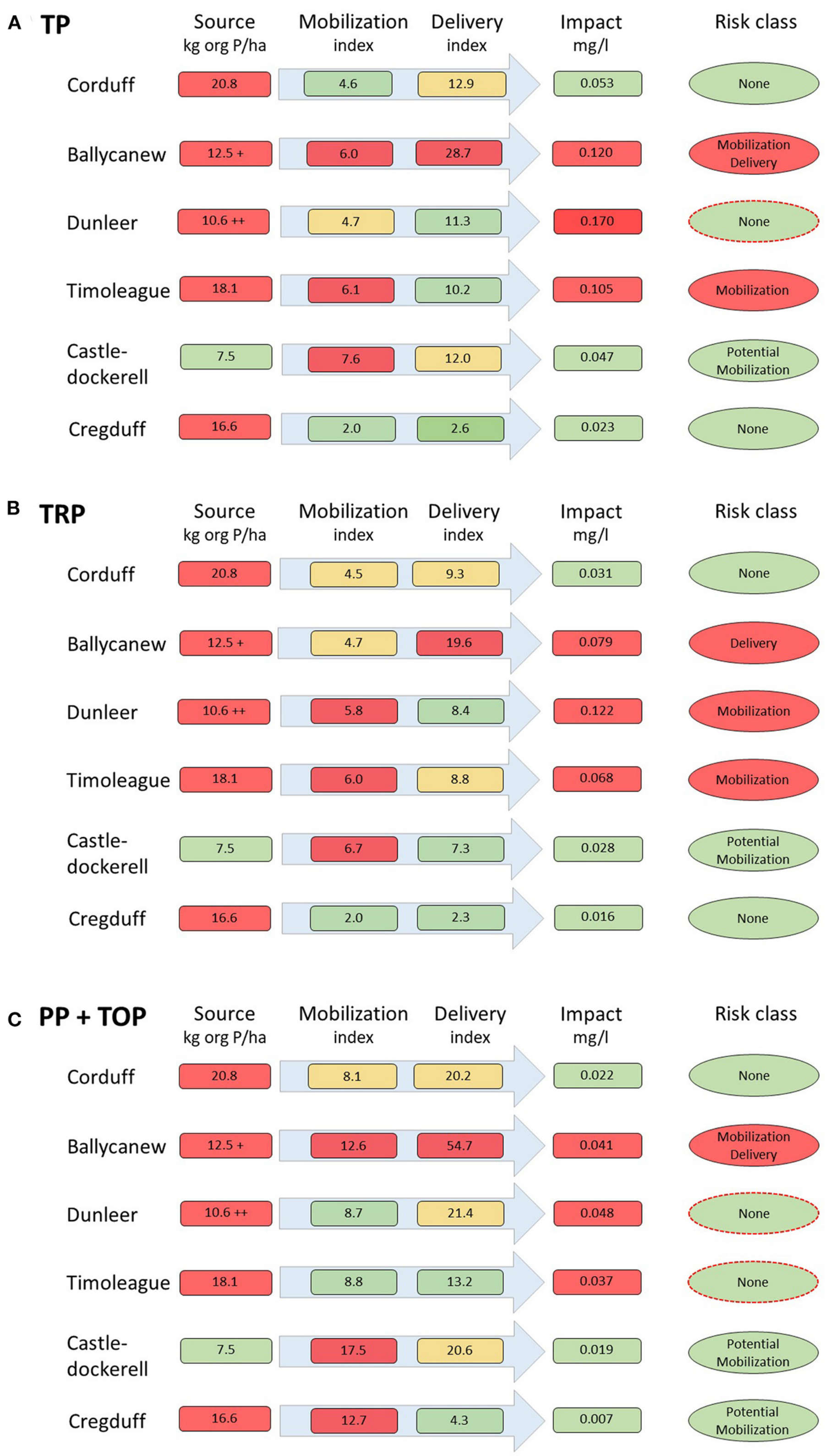


FIGURE 7
The conceptual P transfer continuum model (Haygarth et al., 2005) populated with data on 10-year average P source, *mobilization index*, *delivery index*, P impact (mg/l) and indicated risk class for **(A)** TP, **(B)** TRP and **(C)** PP + TOP. Colour codes: Red, higher than median and average; yellow, near to median and average (within 10%); green, below median and average. The P source is based on average stocking rate. + indicate added organic manure by slurry and ++ indicates added organic manure by slurry and imported manure.

(*Q5/Q95* = 34 and 83% grassland), Ballycanew (*Q5/Q95* = 126 and 77% grassland), and Dunleer (*Q5/Q95* = 61, 34% arable and 44% grassland), all have a high probability of exceeding EQS and high P sources (Figure 3 and Table 1). However, they have contrasting hydrology and land use, and the catchments' propensity to *mobilize* and *deliver* P to the stream was likely to be different for each catchment. The stream P concentrations were therefor likely to be elevated for different reasons.

Most of the increasing temporal trends in Q and P percentiles were found in Ballycanew catchment (Table 3), where there has been both an increase in rainfall and more frequently occurring large rain events (Mellander and Jordan, 2021). There was also an observed drainage intensification in 2016 that resulted in more runoff and negative annual water balances (not shown). This has influenced the catchment hydrology and may explain the increasing trends of high stream flow and the likely increasing trend of median flow. The increase in low and median TP and TRP concentrations, low PP + TOP concentrations, and a likely increase in the median PP + TOP concentrations could be explained by the long-term changes in weather such as the intensified weather as described by the strength of the North Atlantic Oscillation (Mellander et al., 2018). The increase in the average P mass loads in Ballycanew was likely defined by the changes in runoff.

The occurrence and duration of high P concentrations reflected both the different catchments characteristics and weather. Since persistent point sources were not as diluted during low flows in summer (e.g., Shore et al., 2017; Dupas et al., 2018) the duration of high P concentrations was typically longer in the summer months in all of the study catchments, and mostly so in the hydrological flashy catchments with a low baseflow. That seasonality of longer duration of high concentrations in the summer months was more pronounced for TRP which was typically twice as long as for TP in the hydrologically flashy catchments (Figure 4). Higher runoff in winter but higher sources in summer caused more uniform duration of high TP and PP + TOP concentrations throughout the year. The duration of high mass load of P was highly reflected by hydrology and was typically longer in winter and autumn months. The January duration peak in Cregduff corresponded to a time of the year when a larger part of the karst conduit system was active (Mellander et al., 2013). With the impacts of weather patterns from climate change these catchments were exposed to dryer summers and to winters with more frequent large rain events. Due to increased P solubilization following soil drying and rewetting cycles (Turner and Haygarth, 2001) and decreased dilution of P in summer, and more runoff induced P loss in winter, it is likely that the duration of high concentrations of P will increase in summer and the duration of high mass loads of P will increase in winter.

## Mobilization and delivery index

The *P mobilization index* introduced here was expressed as the ratio of high and low P concentrations, reflecting the possible range of concentrations and therefor integrated the catchments process of soil P detachment and solubilization into one number. In a similar manner the introduced *P delivery index* was expressed as the ratio of a range of high P mass load and a range of low P mass loads, reflecting the possible range of P mass load and therefor integrated the catchments connection and retention factors into one number. The ranked order of the indices matched the conceptual understanding of the catchments (Mellander et al., 2018, 2022) and allowed a view of the catchments in terms of both dominating P fraction and transfer processes of P loss. These estimations also provided insights to how stable these processes were over time and if there were any inter-annual trends over the analyzed 10-year period. The development of such indices can only be made with long time series of high frequency water quality and concurrent discharge data. It further requires a good conceptual understanding of several study catchments of different characteristics, to allow for an understanding of how these indices relate to the underlying catchment processes. Further development would benefit from including more catchments of different typologies, management, scales, and from different climatic zones. To increase the applicability it would also be useful to test the method on datasets of lower frequency. Castledockerell catchment, which has a high proportion of arable land-use, had both the highest average P *mobilization index* and the largest inter-annual variability. In such catchments where P is easily mobilized, there will be a strong weather signal with corresponding variability. A large proportion of soil in that catchment were bare in wintertime, coinciding with saturated soils and a number of large and erosive runoff events that can mobilize soil P, and especially PP (Mellander and Jordan 2021). Similarly, it was found that Q 90th PCTL (i.e., Q10) events transported 80% of P in an agricultural headwater catchment in U.K. (Ockenden et al., 2016). This is highly relevant since large autumn and winter rain/runoff events have increased in Ireland in the last decade (Murphy et al., 2018), which may explain both large inter- and intra-annual variability and the increasing trend in TP *mobilization*. Timoleague catchment had high average *mobilization indices* for TP and TRP. This catchment is dominated by iron-rich and well-drained soils that favor P *mobilization* into a soluble form that can easily leach into shallow groundwater, which contributes a large proportion of the total TRP loss at the catchment scale (Mellander et al., 2016) and can therefore be viewed a *mobilization risky* catchment. In Ballycanew catchment the *mobilization index* was relatively high for TP and PP + TOP, but the *mobilization index* for TRP was relatively low. This is likely explained by its high *Q5/Q95* and erosive runoff (Sherriff et al., 2016), and low groundwater contribution (low *BFi*). In the Cregduff karst spring zone the relatively high PP + TOP mobilization indicated a large capacity to remobilize PP + TOP within the karst conduits.

Ballycanew catchment, having the highest hydrological flashiness, also had the highest *delivery index* for all P fractions due to dominating quick surface pathways connecting and transferring P sources to the stream all year round (Mellander et al., 2015). This catchment had three times higher TP loss for approximately the same discharge as Castledockerell, and it also had more than twice as high *delivery index* than Castledockerell, despite the latter having a higher *mobilization index*. These two hydrologically contrasting catchments had a high inter-annual variability in *delivery index* and were found to respond differently to changes in weather (Mellander and Jordan, 2021). The karst spring zone (Cregduff) had both the lowest average *delivery index* and the lowest inter-annual variability. This agrees with previous findings reporting this catchment to have a high P retention capacity of the calcium rich soils and highly buffered hydrology with most of the spring flow occurring during flow events (85–93%) fed by slow flow in the small to medium sized fissures (Mellander et al., 2013).

The catchment's flow regime appeared to be a highly important factor for both the P *mobilization and delivery indices*, and possibly more so than the P sources. In general, the *mobilization indices* were higher for TRP in the groundwater driven catchments with a high *BFi* and the *delivery indices* were higher for TP and PP + TOP in the hydrologically flashy and surface water driven catchments with a high *Q5/Q95*.

## Catchment phosphorus export regime

To understand the increasing trends over 10-years observed in some catchments and for some fractions of P, the catchment P export regimes need to be considered (Minaudo et al., 2019). The C-Q relation can indicate whether a catchment is chemo-static or chemo-dynamic (Goodsey et al., 2009) and can reveal how large flow events may influence the mobilization and delivery of P fractions differently for different catchments (Hashemi et al., 2020). The trends in the indices (Figure 5) were mostly seen in the P fractions that were chemo-dynamic (Figure 6) in some catchments. For example, the chemo-static behavior of TRP and chemo-dynamic behavior of TP and PP + TOP in Ballycanew, Dunleer, and Castledockerell indicated that the high flows were only able to access soluble P sources with limited mobility. By contrast, TP and PP + TOP continued to be mobilized and delivered by more erosive high flow events, suggesting a depletion in these pools of limited mobility. Being able to understand the different sources for mobilization is critical for the development of models and also critical to better assess the efficacy to potential intervention measures. Changes in rainfall/runoff would then likely influence the trends for TP and PP + TOP but not for TRP in those catchments. In Cregduff only the PP + TOP was chemo-dynamic and, as with the high variability in *mobilization index*, this indicated a capacity to remobilize PP + TOP within the karst conduits. However, there was only an increasing trend in TP.

## Identifying the catchment scale *P* loss risk

The developed *mobilization* and *delivery indices* were tested by combining them with information on *P source* and *impact* to estimate the complete *P transfer continuum* (Haygarth et al., 2005) in a matrix (Figure 7). Each part of the continuum was seen as a risk factor where the *source* in conjunction with either the *mobilization* and/or *delivery* need to be elevated to cause an elevated *impact*. This type of screening tool could help to identify the specific or potential type of P loss risk present in a catchment, and could therefore be useful in planning measures for diffuse pollution management.

The screening tool assumed high organic P sources in all catchments except Castledockerell catchment (which has a high proportion of arable land-cover). Despite stocking rates being relatively low in Dunleer, nutrient management was not spatially balanced with P inputs rarely matching the crop and soil P requirements at the field scale, which is largely due to imported manure (McDonald et al., 2019). There were also higher domestic sources of P in that catchment (Shore et al., 2017). In both Dunleer and Ballycanew sources were also considered to be higher due to a longer housing of cattle generating more spreading of manure.

The screening tool reveals that a high *source* did not cause a high impact if the *mobilization* and/or *delivery index* was not high, such as was the case for all P fractions in Corduff (Figure 7). In addition, a high *mobilization* and/or *delivery index* was not enough to cause a high *impact* if the *source* was low, such as was the case for all P fractions in Castledockerell. In the three catchments where EQS were frequently exceeded (Ballycanew, Dunleer, and Timoleague) there were different risks associated to the high impact. Ballycanew was both *mobilization* and *delivery* risky for TP and PP + TOP and *delivery* risky for TRP. Dunleer was only *mobilization* risky for TRP but not for TP and PP + TOP. This mismatch of the tool, indicating no risk while the *impact* was high, may be explained by an underestimation of the *mobilization* and *delivery indices* due to the high point source influence that elevated P concentrations in the low flows. Dunleer is a relatively hydrologically flashy catchment with high P sources, which is likely to be both *mobilization* and *delivery* risky. Timoleague catchment was *mobilization* risky for TP and TRP, in agreement with previous studies (Mellander et al., 2016). That catchment was not determined to be risky for losses of PP + TOP, which could be explained by a relatively high 5th PCTL concentration, likely due to high concentrations of TOP (Fresne et al., 2020, 2022) which were not elevated in the higher PCTLS and thus gave a low *mobilization index*.

The screening tool also indicates the potential risks for P losses in some catchments and could therefore be used to assess if a catchment is sensitive to changes in source pressure (management) and/or runoff (weather). Considering the link of hydrology to the *mobilization* and *delivery* indices, ongoing climate change with more extreme weather events, will likely increase either of these indices in a catchment like Corduff. Since that catchment already has a high source, it would turn the catchment into a high *impact* P loss risky catchment. There was already an existing increasing trend in the TRP *mobilization index* (Figure 5A). Additionally, Cregduff could become a high impact TP and TRP loss risky catchment with an increased *mobilization* and/or *delivery index*. The catchment is further susceptible to changes in PP + TOP due to its chemo-dynamic nature (Figure 6). Castledockerell is a potential *mobilization* risky catchment for all fractions of P. With an increase in source pressure (agronomical intensification) this catchment could become *mobilization* risky with high *impacts*. Due to the chemo-dynamic response of TP and PP + TOP to increased discharge, it is likely that this catchment will also respond to changes in weather in terms of P loss risk.

This screening tool can provide useful information for targeting suitable mitigation methods and further to design these for scenarios of future weather and land use. With more high frequency monitoring of water quality parameters there is potential to link *mobilization* and *delivery indices* to catchments typologies, land use, and climate classes for future risk assessments.

## Conclusions

As a tool to help diffuse P management a new systematic and objective method was introduced to estimate the propensity of P detachment/solubilization into a *P mobilization index* and connectivity/retention into a P *delivery index* at the catchment scale. The approach is based on analyzing 5th, 50th, and 95th percentiles from 10 years of hourly data (Q, TP, TRP, and PP + TOP) monitored in six river catchments with contrasting hydrology and agricultural management across Ireland. The catchments' P transfer processes were integrated into indices which can be used to assess P loss to waters. Estimating these indices over several years provided insights to the stability of transfer processes over time and identified any inter-annual trends. Development of the P *mobilization* and *delivery indices* was only possible due to long-term, and high frequency monitoring of water quality and discharge from catchments of different typologies, together with a conceptual understanding of the catchments.

The catchments' flow regimes were important for both P *mobilization and delivery indices*. Within the six study catchments, the groundwater driven catchments (with *BFi* ranging from 0.73 to 0.82) typically had a higher P mobilization index for TRP (2.0–6.7). The catchments where quick surface pathways were more frequent, with a high *Q5/Q95* (61–126), typically had a higher delivery index for TP (11.3–28.7) and PP+ TOP (20.2–54.7). The export regimes should be considered when interpreting the inter-annual trends in the P *mobilization and delivery indices*. Increasing or decreasing trends were mostly found in catchments and P fractions with a chemo-dynamic response in the Q-C relation.

The P *mobilization* and *delivery indices* were used to quantify the components of the P transfer continuum as a simple screening tool to compare P loss risks in the catchments. The dominating risk factor and potential risk factor in a catchment could be identified. Such tools can provide useful information for targeting sites for suitable mitigation methods and further to design these for scenarios of future weather and land use. Further development of the indices would benefit from including more catchments of different typologies, management, sizes, and from different climatic zones. Such developments would indicate the robustness of the method, and it would also be useful applying it on a dataset of lower frequency.

## Data availability statement

The datasets presented in this article are not readily available because of data confidentiality. Requests to access the datasets should be directed to the corresponding author.

## Author contributions

P-EM contributed to the conceptualization, methodology, and writing. All authors have contributed to the analysis and writing, and have approved the submitted version.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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