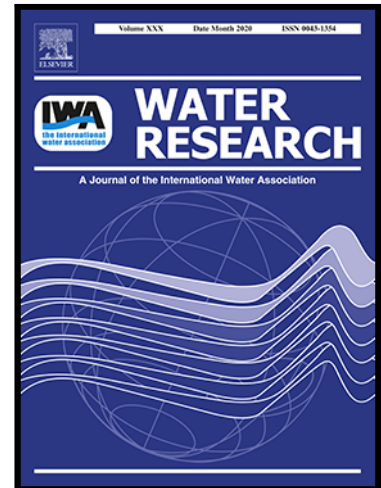


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The spatial and temporal dynamics of sediment phosphorus attenuation and release in impacted stream catchments

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Highlights

- The space-time dynamics of streambed sediment phosphorus (P) was studied in detail
- Labile P in sediments was most mobile in storms and chemically quick to recover
- Phosphorus Exchange Potential was dynamic in space and time but rarely saturated
- P attenuation/release from specific sediment P fractions were important processes
- Chemical bioavailability of mobilised labile P from sediments is a research gap

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The spatial and temporal dynamics of sediment phosphorus attenuation and release in impacted stream catchments

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Abstract

Sediments can attenuate phosphorus (P) from overlying water and reduce trophic status in zero and first order ditches and streams. These features can be considered as intermediate mitigation features between P mobilised from land, and onward delivery to river systems, if the risk of chemical P release from sediments is minimal. However, risk assessments are rarely based on temporal scale dynamics and especially at fine scale in both sediment and water column environments. In this study, in eutrophic stream catchments, bed sediments were tested fortnightly and spatially over one year for EPC_0 (to derive phosphate exchange potential—PEP) and for P across a spectrum from labile to recalcitrant fractions. At the same time stream discharge and P concentrations were measured synchronously at high frequency and resolved to 1-hour intervals and indicated high water quality pressures at all flow rates. PEP indicated spatial and temporal changes most likely caused by periods of source disconnection/reconnection and sediment mobilisation during storm events, moving from periods of high attenuation potential to near saturation. Despite these spatial and temporal changes, PEP did not indicate much potential for chemical P release from the sediments (distributing mostly below or close to zero). However, this may be a misleading risk assessment by itself as physical P release, especially of the labile bicarbonate-dithionite (B-D) P fraction of sediments, was a more dominant process mobilised during storm events reducing by up to 84% during a succession of summer storm events. The total P and total reactive P loads monitored leaving the catchments were coincident with these changes. The specific downstream trophic effects of this episodic P release will need to be assessed in terms of its bioavailability, in combination with other more noted diffuse and point P source processes.

Key words: Phosphorus, fractionation, EPC_0 , phosphate exchange potential, stream sediments, water quality

1. Introduction

Research into the dynamics and fate of land to water nutrient transfers is extensive and related to the ecological and economic impacts of water pollution (Powers et al., 2016). Phosphorus (P) is a particular focus due to its presence in wastewater discharges to aquatic systems and in both diffuse and incidental runoff from agricultural soils (Ott and Rechberger, 2012). This can result in river and lake eutrophication impacts (Correll, 1998). As a framework for these conditions and processes, Haygarth et al. (2005) proposed the P transfer continuum: source – mobilisation – delivery – impact. The model is a useful means of putting into context and linking together catchment P sources through indeterminate combinations of transfer and cycling processes to the eventual impact of nutrient enrichment on water quality at various scales (e.g., Forber et al., 2018; Vero and Doody, 2021).

In the agricultural landscape, rural streams and open ditches (zero to first order) constitute an extensive drainage network which can be regarded collectively as a conduit of P transfer into receiving waterbodies (Jordan et al., 2012; Bieroza and Heathwaite, 2015; Grewal et al., 2020). However, bed sediments in rural streams and ditches can retain P through settlement and adsorption to the physical and chemical constituents of fine sediment (Sherriff et al., 2016), and this can potentially amount to significant quantities over prolonged periods of P loading from fields and rural point sources. Moreover, this phenomenon has been proposed as a mitigation option in some circumstances (Kleinman, 2007), classifying ditch networks into their likelihood for attenuating P into bed sediments, for example based on channel gradients (Shore et al., 2015). Others have also indicated how P attenuation processes in stream bed sediments can offset eutrophication risk at certain flow regimes, even at quite large scales (Jarvie et al., 2005; Ensign et al., 2006; Roberts and Cooper, 2018; Simpson et

al., 2021). Further studies review how this buffering can be exploited by physical, biological, or chemical augmentation of the bed sediment environment (Hodaj et al., 2017; Kalcic et al., 2018; Nsenga Kumwimba et al., 2018; Mohd et al., 2022).

Nevertheless, storage of P as an intermediate step between diffuse mobilisation (or point source inputs) and final delivery in ditches, streams and rivers is described as a legacy P store by Sharpley et al. (2013). Such stores have been described for soils where P inputs have been removed and the legacy continues to potentially transfer P for considerable periods (Schulte et al., 2010). Similarly, the legacy risk of P from bed sediments have been described in the soluble phase in stream water by exceeding sediment equilibrium P concentrations (EPC_0) during low flow periods (Moloney et al., 2020), or by physical removal during high flow periods (Dorioz et al., 1989).

There is clearly no one size fits all to describe these processes, and Simpson et al. (2021) provide a comprehensive review and meta-analysis of EPC_0 with overlying stream dissolved reactive P (DRP) data from around the world to help with risk/utility assessments. They used the “phosphate exchange potential” (PEP) as a summary to reflect the differences in magnitude between EPC_0 and DRP (i.e., when $EPC_0 > DRP$, bed sediments are buffers and restrict DRP movement into overlying water), and that this rarely reaches zero. The authors acknowledge that these processes can also be interrupted or reset by hydrological events but still found EPC_0 a reasonable predictor of DRP following a scouring flood event in a more regional study (McDowell et al. 2019).

Within this process of P attenuation and release (chemical or physical) is the nature of the P within bed sediments and particularly labile and recalcitrant fractions. These may also have a modifying effect on the strength of P attenuation/release although it is rare to find research reporting the changing nature of these conditions, with spatial surveys more commonly reported (e.g., Lannergård et al., 2020). Less common still is research on the fine temporal combination of chemical P buffering process, P lability/recalcitrance of sediments, and the hydrological dynamics of P in the stream/river system over longer, seasonal time scales.

Such datasets are difficult to bring together in single studies as they are likely to be used in isolation for different objectives. Here archived data were used from published and unpublished research related to BlackwaterTRACE (Trans-boundary Action for Community and Environment—2004 to 2010), a research and action initiative on diffuse and point source pollution in the cross-border area of Ireland (Jordan et al., 2008). Using these datasets, the aim of the current study was to fill a knowledge gap on the dynamic nature of sediment-water P interactions in highly impacted catchments. The objectives were to, 1) investigate fine temporal P attenuation and release processes as seasonal intermediate steps in the nutrient transfer continuum and, 2) place these results into an existing or modified conceptual model of bed sediment P risk/utility for application in eutrophication management.

2. Methods

2.1 Study area and datasets

The Irish cross-border Blackwater River drains approximately 1,480 km² of mostly agricultural land in north-central Ireland and is one of the six main inflowing rivers to the hypertrophic Lough Neagh (354 km²). Land use is mostly grazed pasture and silage meadow for dairy, beef, and sheep enterprises. Iron/aluminium rich Gleysols have developed on a post-glacial drumlin landscape, with humic soils in inter-drumlin swales (Jordan et al., 2008). Extensive land drainage operations in the 1970s and 1980s deepened and widened main river channels and facilitated an extensive network of open ditches and small streams (zero and 1st order streams). At all scales, this provides a flashy storm hydrology and suppressed baseflows (Cruickshank, 1997). Three BlackwaterTRACE study catchments were established in Co. Tyrone, Co. Monaghan and Co. Armagh, of 5.0 km², 6.1 km², and 3.1 km², respectively, with a common experimental and monitoring design.

The BlackwaterTRACE datasets were gathered between approximately 2005 and 2010 with information on land use and hydrometeorology, soil and sediment P dynamics, sediment microbial and steroid patterns, sediment P fractionation and buffering, and high-temporal resolution P data from bankside analysers. Core motivations for these data were to identify the major sources of diffuse and point source P pollution in space and time at catchment scale (Jordan et al., 2005; 2007; Arnscheidt et al. 2007), and to mitigate those sources (Macintosh et al., 2011; Campbell et al., 2015). Archived data provided a common year from 1st April 2008 to 31st March 2009 (i.e., two water half-years) where published synchronous hydrological and water quality data could be combined with unpublished sediment P

fractionation and EPC_0 measurements at three sites in each of two of the study catchments (Co. Monaghan and Co. Armagh, Fig. 1).

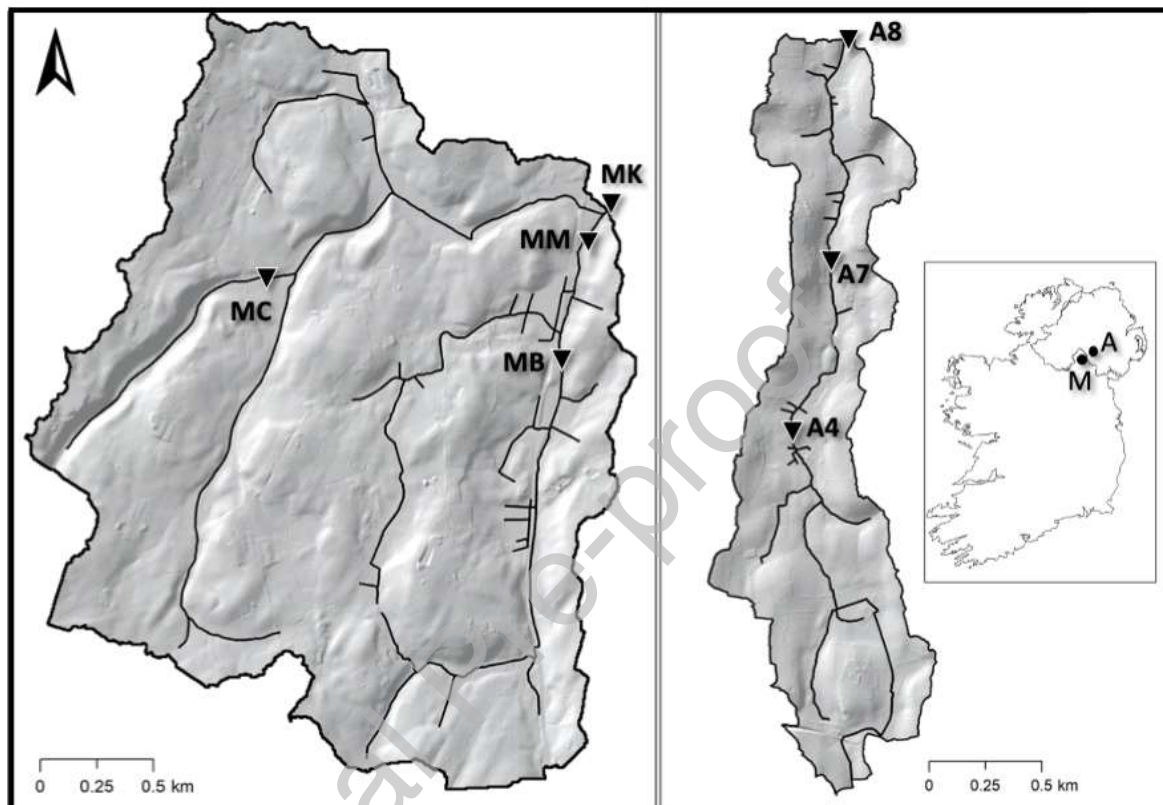


Fig. 1. Catchment maps for Co. Monaghan (M) and Co. Armagh (A), and location in the Irish border area. Solid black lines indicate the stream network and inverted black triangles indicate sample sites. Sites MK and A8 at the catchment outlets are where synchronous hydrological and water quality (P) data were captured at high resolution. Sites MM, MB, MC and A8, A7, A4 are where bed sediment and water column P data were gathered.

2.2. Hydrometeorology and water quality

Methods for hydrological and water quality monitoring data are described extensively elsewhere (e.g., Jordan et al., 2007; Jordan et al., 2013; Campbell et al., 2015) and

summarised here. At the outlets of each catchment, water level was measured at 1 min intervals and averaged in a 15 min filter (Thalimedes, OTT, Germany). Measurements were calculated to discharge using combinations of area-velocity gauging (Nautilus, OTT, Germany) and *in situ* ultrasonic depth-velocity measurements (Starflow, Streamline Measurements, UK). Rainfall data were measured in the centre of the Co. Monaghan catchment using a tipping bucket rain gauge (ARG100, EML, UK), which is 20 km from the centre of the Co. Armagh catchment. As a reference point, open-source rainfall data for the Blackwater River catchment were compared for the study year and for a ten-year period (NRFA, 2022).

Continuous measurements of P were also taken at the outlets using a bankside analyser (Phosphax Sigma, Hach, Germany). Briefly, water is extracted under positive pressure (Sigmatax, Hach, Germany), homogenised by ultrasound, and aliquots delivered for processing. The time-step was set to six samples per hour with alternative steps providing a digest of the sample before analysis by colorimetry (Eisenreich et al., 1975—DIN EN 38405 D11). This provided alternate total P (TP – unfiltered, digested) and total reactive P (TRP – unfiltered, undigested) concentrations within a range of 0.010 mg L^{-1} to 5.000 mg L^{-1} (Jordan et al., 2007).

2.3. Sediment sampling

Sediment sampling sites were located following field surveys of sediment accumulation (Supplementary Material—Fig. SM1). At each site (Fig. 1), water samples for DRP were collected in sterilised 500 ml polyethylene bottles at the upstream point of the sediment sampling site. Stream bed sediment was then sampled from the top 1 cm of the sediment profile using a sterile 50 ml plastic syringe

(Plastipak, BD, Switzerland) with the nib removed to precisely control the sampling depth. This was done across the width of the stream channel and further upstream (typically over a range of 2 – 10 m) at approximately 10 locations, without further disturbance of the sediment surface. The approximate 150 ml of composited samples per site were retained in re-sealable polythene bags, and double-bagged.

The water samples and composite sediment samples were placed in an ice box, which after transit were stored in the refrigerator at 4 °C. Light and air were excluded throughout the transport and storage process to minimise any potential biological activity. Sediment sampling took place over a 12-month period from the start of April 2008 to the end of March 2009, at regular intervals of 2 weeks.

2.4. Laboratory methods: EPC_0

Phosphorus sorption experiments, to determine sediment EPC_0 , were carried out in batches (Jarvie et al., 2005). Wet sediment was thoroughly homogenised before being used. In the sorption experiments, for each sample, six identical sediment sub-samples were weighed into clean, dry 250 ml polypropylene bottles (Nalgene, TFS, UK), according to the wet sediment mass equivalent to 0.50 g in dry mass. The P solutions used in the experiments were non-acidified KH_2PO_4 solutions of six concentrations in a matrix of 2 mM calcium chloride solution ($CaCl_2$, AnalaR, BDH, UAE): 0.000, 0.125, 0.250, 0.500, 0.750 and 1.000 mg P L⁻¹.

According to the definition of EPC_0 , DRP concentrations in solution with sediment were measured both before and after a 24 hour reaction period; approximately 40 ml

of each solution was filtered (0.45 μm) and the supernatants were tested for DRP by the spectrophotometric method of phosphomolybdate-blue (Murphy and Riley, 1962).

2.5. Laboratory methods: sediment P fractionation

The purpose of investigating sediment P fractionation is to distinguish and quantify fractions of P associated with lability and recalcitrance, and thereby to provide insights into the potential for P retention and/or release under suitable conditions (e.g., with regard to pH and redox conditions) (Sun et al., 2009). The P fractionation method used was a modified Psenner sequential extraction scheme, based on the work of Psenner and Pucsko (1988) and Hupfer et al. (1995) and compared with a total acid digest (Bock, 1979).

A wet and dry sediment mass ratio was established with each composite sample for onward calculations. Using these relationships, 2-2.5 g wet sediment was weighed into clean, dry centrifuge tubes for reaction and subsequent separation in duplicate. Sequential fractionation was then carried out using the reagents that propose a series of P fractions depending on background chemistry and redox conditions (Table 1). Tubes were shaken for set reaction times, centrifuged, the supernatant taken for P analysis and the step repeated for the next fraction. Residual P was measured on residual sediment pellets preserved at the end of the Psenner fractionation procedure. The sum of all Psenner fractions was then compared against a total digest of 0.3 g dried sediment samples (Bock 1979—sequential heated digest of HF, HNO₃ and HClO₄ concentrated AnalaR acids, BDH, UAE). Phosphorus in each fraction was determined by the same spectrophotometric phosphomolybdate-blue method.

Table 1. Method used for sequential P fractionation of bed sediments based on a spectrum from labile to recalcitrant fractions.

Method	Extractants	Reaction time	Proposed P fractions	State
Hupfer <i>et al.</i> (1995), after Psenner and Pucsko (1988)	NH ₄ Cl (1 M)	30 mins	Loosely adsorbed P	
	Bicarbonate-dithionite (BD)	60 mins	Reductant-soluble P	
	NaOH (1 M)	16 hours	Fe-P and Al-P (reactive P); organic P (non-reactive P)	
	HCl (0.5 M)	16 hours	Ca-P	
	Residual	Digested	Refractory P	

The sediment P concentration fractions, in units of $\mu\text{g P g}^{-1}$ (dry mass), were calculated as:

$$P_{sed} = \frac{c_{ext} \cdot V_{ext}}{m_{ws} \cdot r_{dry}} \quad (\text{Eq. 1})$$

Where P_{sed} is the sediment P concentration in a given fraction ($\mu\text{g P g}^{-1}$), c_{ext} is the solution P concentration in the corresponding extract (mg P L^{-1}), V_{ext} is the volume of the extract (L), m_{ws} is the wet sediment mass (g), and r_{dry} is the dry sediment mass ratio (dimensionless).

2.6. Data handling and analysis

Hydrology and water quality data were quality controlled (automated filtering of below and above range values, and visual checking/editing of the time-series) and

synchronised to an hourly time-step. Discharges were normalised to catchment area (mm hr^{-1}) and the product of discharge and P concentration provided normalised load data (kg ha^{-1}). Rainfall was synchronised to a daily time-step, which was the coarsest resolution from the two datasets.

To assess for P concentration pressures delivered from the catchment and through the stream systems, and as a potential P source to the bed sediments, hourly hydrological data were reduced to thirteen percentile discharge ranges (i.e., 1, 5, 10, 20... 80, 90, 95, 99) and the median P concentration in each percentile range was calculated. Relationships were explored with linear regression (Microsoft Excel and Peltier 4.0 add-in).

The EPC_{sat} of sediments was calculated following Jarvie et al. (2005) to determine the number of sample occasions EPC_0 could be confidently defined as a sediment P source or sink by being outside a range of $\pm 20\%$, which approximates the equilibrium state. To assess for the magnitude of these occasions, the PEP of EPC_0 and DRP was calculated (Eq. 1) at all sites and occasions following Simpson et al. (2021):

$$\text{PEP} = \log_{10}(\text{EPC}_0) - \log_{10}(\text{DRP}) \quad [\text{Eq.1}]$$

Locally weighted smoothing (LOESS) regression was used to visualise these magnitudes and trends through the year.

3. Results

3.1. Hydrometeorology

Time-series of rainfall and discharge are shown in Figs. 2a and 2b. Over the 12 month monitoring period, 1,004.8 mm and 981.2 mm of rainfall was measured in the Co. Monaghan and Blackwater River catchments, respectively. Thirty eight percent (381.8 mm) and 36 % (353.2 mm) of the rainfall fell in the meteorological summer period of the year (June, July, August), respectively, with a particularly wet August 2008 (197.8 mm and 173.4 mm, respectively) and influenced by very large storm events during 16-19th August 2008 (50.6 mm and 34.7 mm, respectively) that was preceded by several wet weeks. Ten-year rainfall records for the Blackwater River indicated, on average, an annual rainfall of 1,024 mm but with 24 % (245.8 mm) as summer rainfall (2000 to 2010; NRFA, 2022—data not shown). The results of this study have, therefore, to be taken in this context and allowing for a wetter summer.

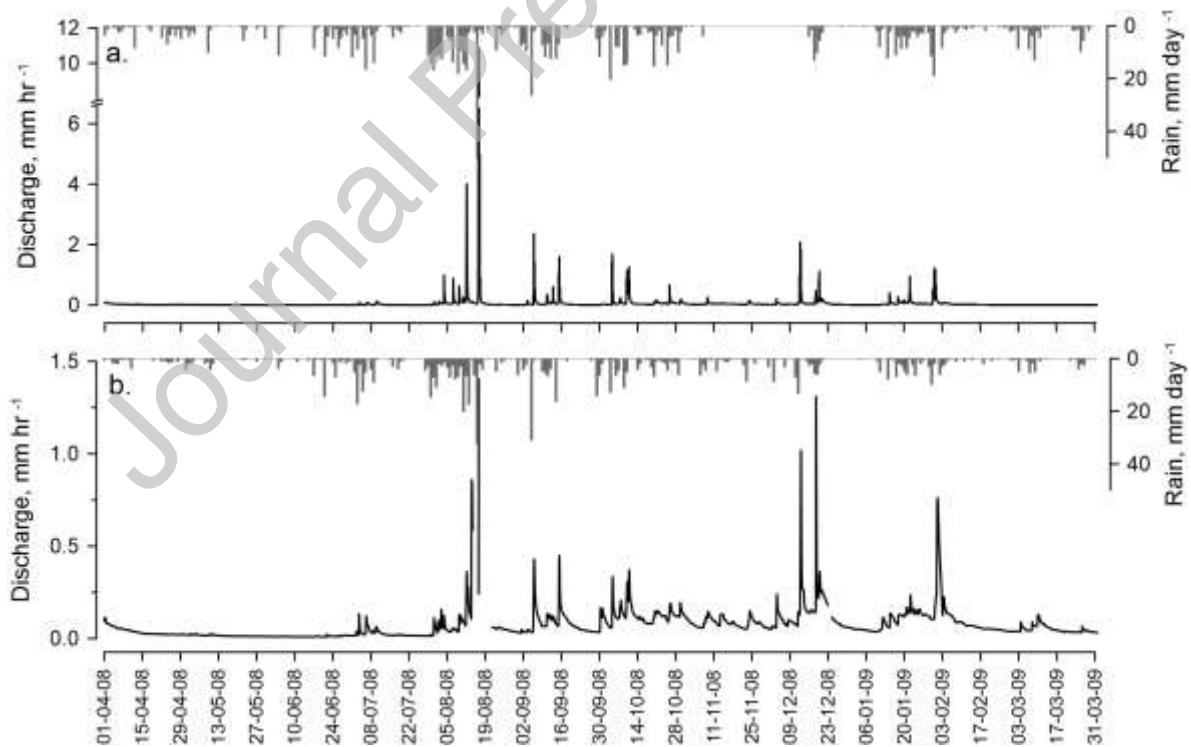


Fig. 2. Normalised discharge for the period 01/04/08 to 31/03/09 period in the Co. Monaghan (a) and Co. Armagh (b) catchments. Rainfall was measured within the Co.

Monaghan catchment. Co. Armagh rainfall was taken from records covering the whole Blackwater River catchment.

Normalised discharge over the 12 month period was 563.0 mm and 617.3 mm for Co. Monaghan and Co. Armagh, respectively. Some periods of missing discharge data from both catchments precluded an exact comparison, although the summer periods recorded 38 % of accumulated discharge in Co. Monaghan and 13 % in Co. Armagh. This compared with a 10 year annual discharge of 606 mm at a wider 970 km² hydrometric station on the Blackwater River, and 12 % of this during the summer period (2000 to 2010; NRFA, 2022).

3.2. Phosphorus water quality

Time-series of P concentrations for both catchments are shown in Figs. 3a and 3b. Following quality control, out of a possible 8,761 hourly datapoints, coverage of synchronous discharge and P concentration pairs was TP—83 % and TRP—83 % for Co. Monaghan, and TP—77 % and TRP—76 % for Co. Armagh. Concentrations of TP and TRP ranged from approximately 0.005 mg L⁻¹ (assumed as half the LoD of the instrument), to almost 3 mg L⁻¹. Accumulated TP loads reached up to 1.91 kg ha⁻¹ yr⁻¹ in Co. Monaghan and almost 0.92 kg ha⁻¹ yr⁻¹ for Co. Armagh (likely to be underestimated due to the lower percentage paired data coverage).

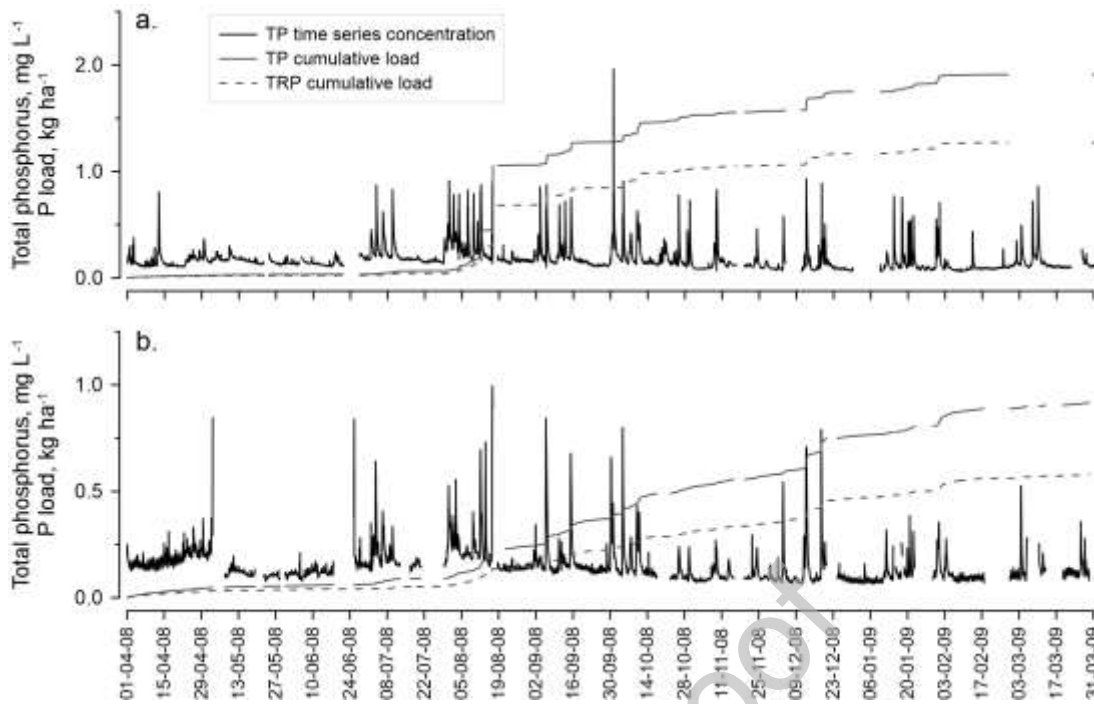


Fig. 3. Time-series of P load and accumulated loads for the Co. Monaghan (a) and Co. Armagh (b) catchments, respectively.

The percentile discharges and associated median P concentration in each range are shown in Figs. 4a and 4b. These indicate strong relationships in both catchments and show several important features. First, is a concentration minimum feature in the fitted orthogonal polynomial regression (black arrows in Figs. 4a and 4b) normally interpreted as a potential change point in load apportionment models (Bowes et al., 2008). This change point describes the onset of strong flow dependent diffuse P transfers (to the right of the black arrows), and loss of dilution (to the left of the black arrows) as point sources or shallow groundwater P pathways become dominant when discharges diminish to lower flows (Greene et al. 2011; Crockford et al., 2017; Dupas et al., 2018). However, this latter flow independent concentration state also indicates a maximum concentration in these streams (white arrows in Figs. 4a and 4b). To the left of these points, discharges decrease to extreme baseflows, and concentrations

decrease to other minima. The model fits in Fig. 4a (Co. Monaghan) filter out a datapoint offset from the main trend at this low flow maximum but this is likely to be spurious for this study year. For example, an analysis of the five-year dataset for the catchment shows the same strong relationship (Fig. SM2). These conditions are interpreted as a loss of connection from P sources, as streams and ditches become ephemeral (zero order) in the extreme headwaters.

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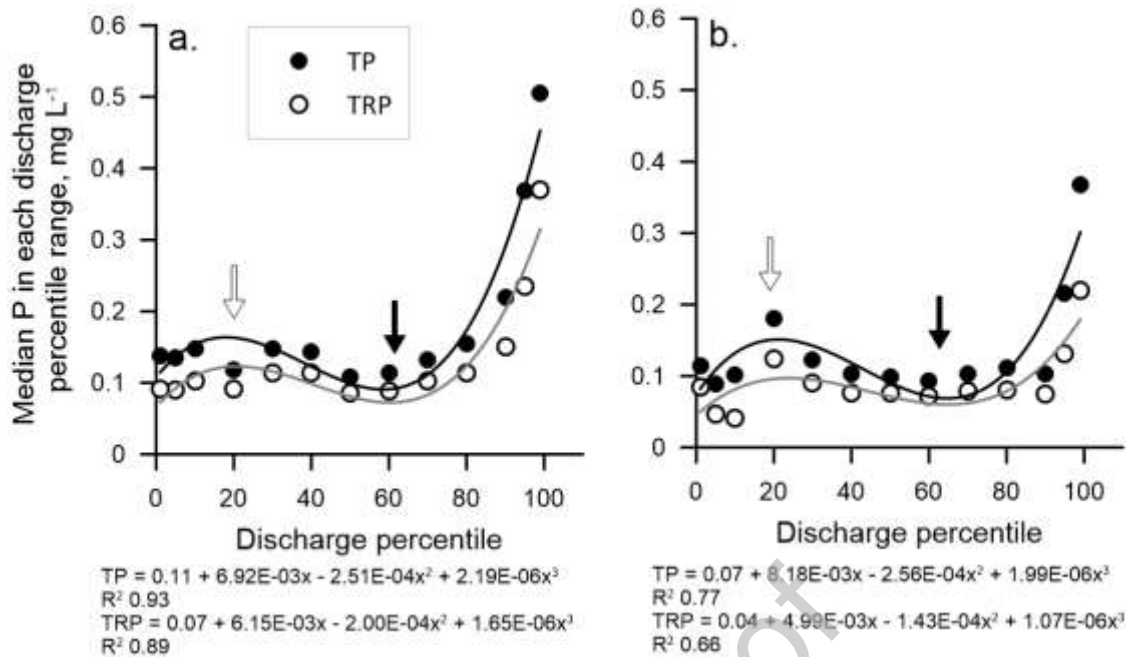


Fig. 4. Discharge percentiles and the median P concentration (TP black circles; TRP white circles) in each percentile for Co. Monaghan (a) and Co. Armagh (b) catchments, respectively. Data are fitted with orthogonal polynomial regressions (TP black; TRP grey). Black arrows indicate a potential change-point between diffuse (right of arrow) and point (left of arrow) source pressures. White arrows indicate a further change point where point sources become disconnected (left of white arrow) at extreme low flows.

Septic tank systems have been implicated as headwater P sources in previous work (Macintosh et al., 2011) although disconnection from other rural points sources or P rich shallow groundwater may also be influential (e.g., Shore et al., 2017; Dupas et al., 2015). Nevertheless, as the decrease in concentration patterns at extreme low flows is captured at the catchment outlets, there is an early interpretation of the role of bed sediments during these extreme low flow conditions. First, there is indication that bed sediments are not acting as a source to replace theoretical disconnection from those other remote sources. Second, P sources still connected to extreme low flows

may be mediated by the bed sediments, hence reducing concentrations, and acting as a sink. Despite this, P concentrations at low flows were high and in ranges normally associated with chronic eutrophication impacts (Jordan et al., 2007). For example, Co. Monaghan 50th to 1st percentile low flow discharges had median TP and TRP concentrations of 0.137 mg L⁻¹ and 0.092 mg L⁻¹, respectively. Similar low flows in Co. Armagh had median concentrations of 0.103 mg L⁻¹ and 0.092 mg L⁻¹, respectively. These were combined with the higher flow P concentrations from acute events as noted in Figs. 3a and 3b, and 4a and 4b showing that, overall, the catchments had heavy water quality pressures.

3.3. EPC₀ state and trends

Following quality control after batch experiments, out of a possible 138 EPC₀ and DRP pairs, 128 were tested for EPC_{sat}. This test indicated that 117 pairs were outside of the ±20 % threshold proposed by Jarvie et al. (2005) and so more certain of bed sediments acting as potential sources or sinks of P to or from the overlying water column, respectively. Of the 117 pairs, 109 were less than the 20 % threshold and 8 were above the threshold indicating a mostly sedimentary P sink over the one year sampling period. The data are shown in Figs. 5a and 5b as standard scatterplots compared against a 1:1 line (i.e., data above the line consider the sediments acting as a potential P sink from the water column). Also shown are the data from each site/catchment as box plots and the range of differences between EPC₀ and DRP over the period (Fig. 5c).

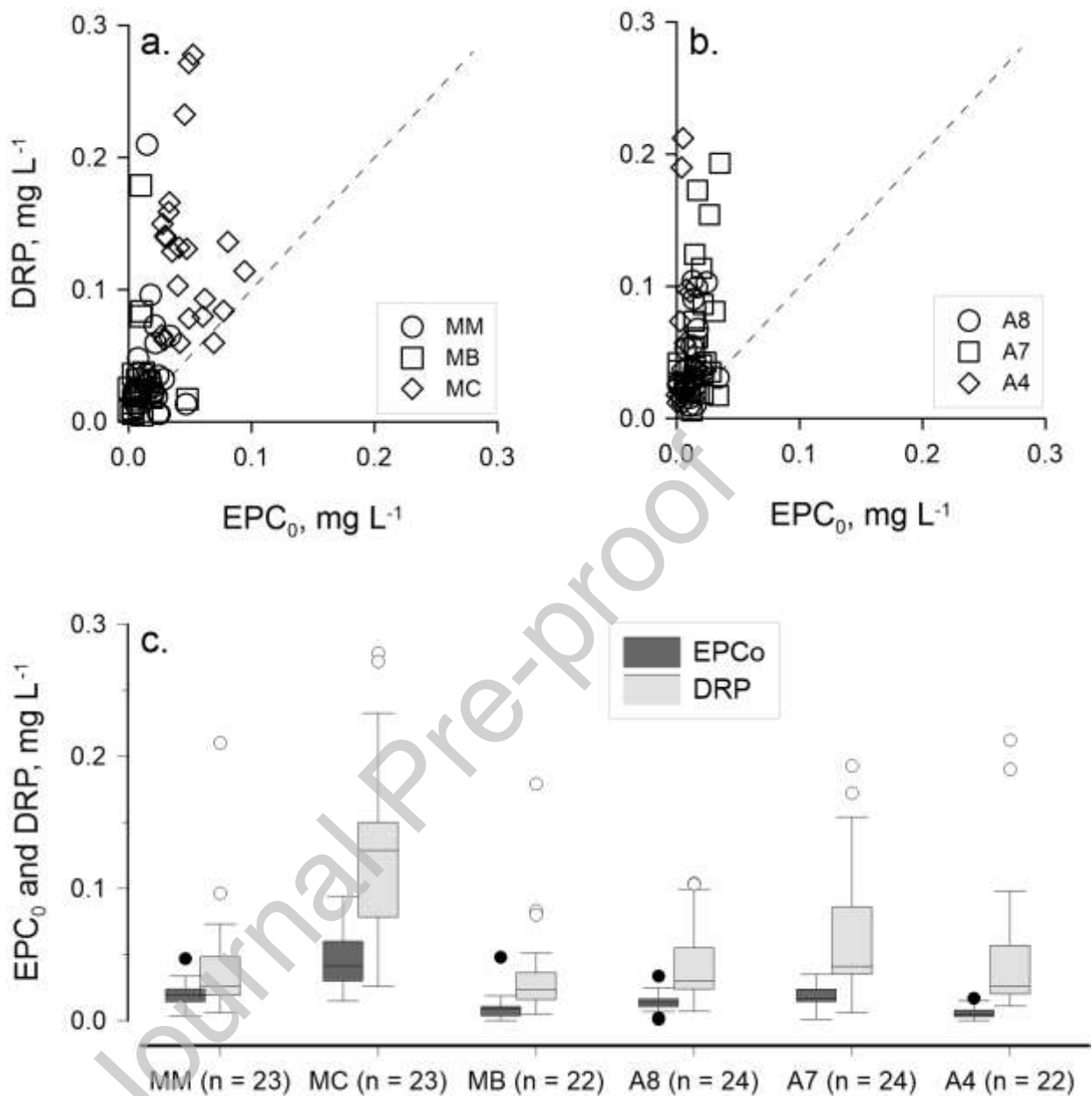


Fig. 5. Scatter plots of EPC₀ and DRP concentration, against 1:1 lines for the Co. Monaghan (a) and Co. Armagh (b) catchment sites. These data are also collated by catchment site as box-whisker plot ranges (c) indicating a mostly sedimentary P sink over the one year sampling period. Whiskers are calculated as 1.5 * interquartile ranges, and outliers (circles) are greater than these values.

The PEP provides an indication of the magnitude and range of differences of EPC_0 and DRP relationships and, as the dataset is large, this can be plotted over time to assess seasonal trends with other time-series parameters. Figs. 6a and 6b show PEP evolution in bed sediments for all sites and both catchments and which is better visualised using a LOESS regression ($\alpha = 0.33$; 8 points for the moving regression). Also shown are the TP time-series for both catchments.

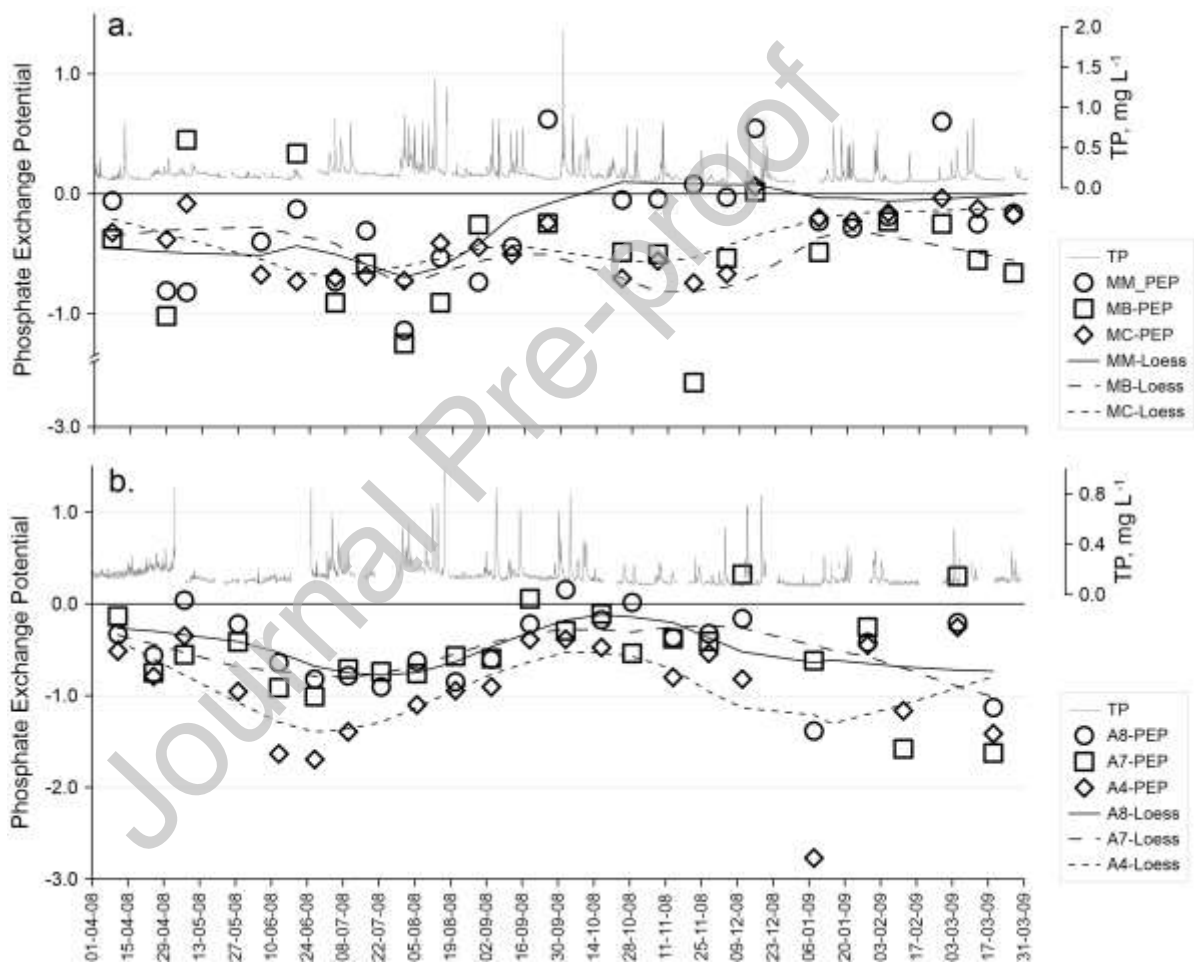


Fig. 6. Phosphate Exchange Potential (PEP) in bed sediments (with stream TP concentration as context), with PEP trends shown as LOESS regressions in the Co. Monaghan (a) and Co. Armagh (b) catchment. More negative PEP values indicate a higher magnitude of P attenuation, and vice versa.

At sites close to the outlets in both catchments (MM and A8), a change in PEP toward zero (equilibrium) is clear in August-September 2008 following a sustained period of increased P concentrations (and as noted in the start of stepped change in cumulative P load, Figs. 3a and 3b). This declines again in Co. Armagh and is approximately similar for the other two sites throughout the year. In Co. Monaghan, this seasonal change in PEP remains close to zero or periodically/slightly above zero for the rest of the year. The two upstream sites in this catchment (MB and MC) followed a similar PEP evolution until August-September 2008 and then diverged albeit with a further increase toward (but not above) zero for MB in the post January 2009 period.

Viewed in isolation, state, magnitude, and trends in EPC_0 show a dynamic picture across the sampling year where stream bed sediments fluctuate from a condition of chemical P sink to periods of saturation. Additionally, for part of the year at least, EPC_0 indicates sediments close to becoming a P source to the water column (i.e., PEP close to zero, but within the $\pm 20\%$ EPC_{sat}).

3.4. Sediment P fractionation

The sum of the sediment Psenner P fractionation results was compared with the sediment TP determined by sequential acid digestion (Bock, 1979) (Table 2). Overall, with a median Psenner recovery range of 102 – 112 %, recoveries were reasonable when considering the stepped nature of fractionation using this method using multiple reagents and potential for uncertainty.

Table 2. Comparison of the sum of Psenner P fractionations and TP by total digestion at each catchment site.

Site	Psenner sum TP, $\mu\text{g P g}^{-1}$		Sediment TP by digestion, $\mu\text{g P g}^{-1}$		Psenner recovery rate, %			
	median	IQR	median	IQR	median	IQR	min	max
MM	513	232	484	186	111	9	95	118
MB	467	240	524	252	105	17	83	127
MC	1742	1667	1914	1383	104	15	90	121
A8	492	149	490	127	104	13	82	118
A7	1272	362	1135	328	102	16	87	128
A4	793	393	630	258	112	18	82	131

The sediment P fractionation ranges are summarised in box whisker plots in Fig. 7 as the proportion contribution of each fraction to the total at each site. In terms of the median concentrations, the potentially labile BD-TP ($197 - 1,047 \mu\text{g P g}^{-1}$) accounted for approximately half of the sediment TP concentration at each of the six sites ($467 - 1,742 \mu\text{g P g}^{-1}$). This indicates a potential for soluble P release under oxygen depletion from this fraction and particularly under low flow and warm conditions (Jarvie et al., 2005). BD-TP was also considerably more than the second largest fraction, which was HCl-TP or NaOH-TP ($97 - 273 \mu\text{g P g}^{-1}$) and had by far the largest inter-quartile range ($72 - 1,395 \mu\text{g P g}^{-1}$). This is explored more as time-series in Figs. 8a, 8b and 8c, and Figs 9a, 9b and 9c. Here the development of total and labile to recalcitrant fractions are shown alongside the accumulating TP load as measured at the catchment outlets (MM and A8). Using MM as reference (Fig. 8a) sediment TP increased during the early summer and peaked at $971 \mu\text{g P g}^{-1}$ sampled on 31 July. During this process, the top half of the graph suggests that the largest fraction, BD-TP, perhaps alongside

most other fractions, saw some growth to contribute to the TP increase. However, the bottom half shows clearly that in fact the contribution ratio of BD-TP remained fairly stable, within the range of 48.5% – 55.0%. In contrast, after high discharge events in August (including the highest of the year), sediment TP rapidly declined and apparently every fraction reduced in concentration terms, but in contribution ratio terms, the main BD-TP fraction had the largest loss. The two samples on 29 August and 11 September 2008 with the lowest sediment TP concentrations of $240 \mu\text{g P g}^{-1}$ and $242 \mu\text{g P g}^{-1}$ also had the lowest BD-TP contribution ratios of 36.7% and 24.1% respectively. As sediment TP subsequently recovered to $363 \mu\text{g P g}^{-1}$ on 25 September and then $429 \mu\text{g P g}^{-1}$ on 24 October, the BD-TP contribution ratio also increased markedly to 40.8% and then 46.2%, approaching the median of 50.4% and recovering to pre-storm levels. Similar patterns of TP and fraction build up and decline were noted in the Co. Armagh catchment (Fig. 9a as reference) and elsewhere at other sites in each respective catchment, but not necessarily synchronous with the two outlet sites.

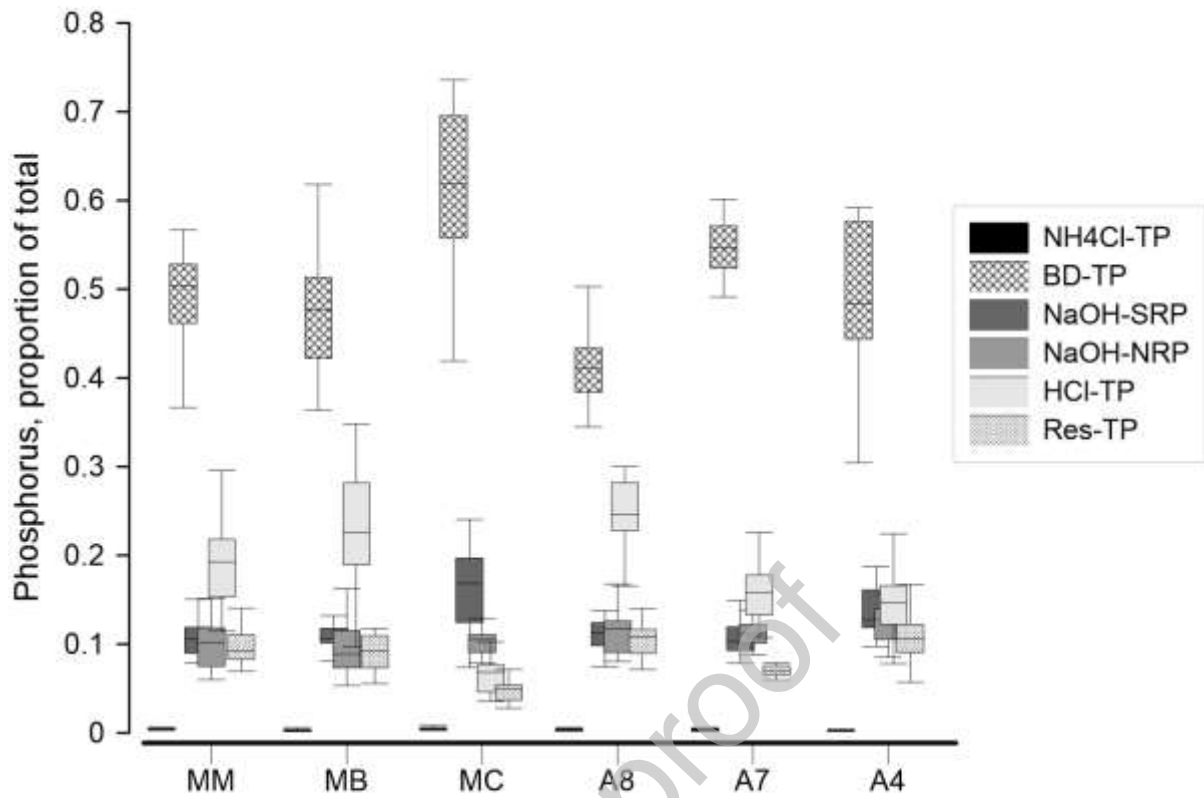


Fig. 7. Box-whisker plots of Psenner P fractions at all catchment sites shown as a proportion contribution to the sum of fractions.

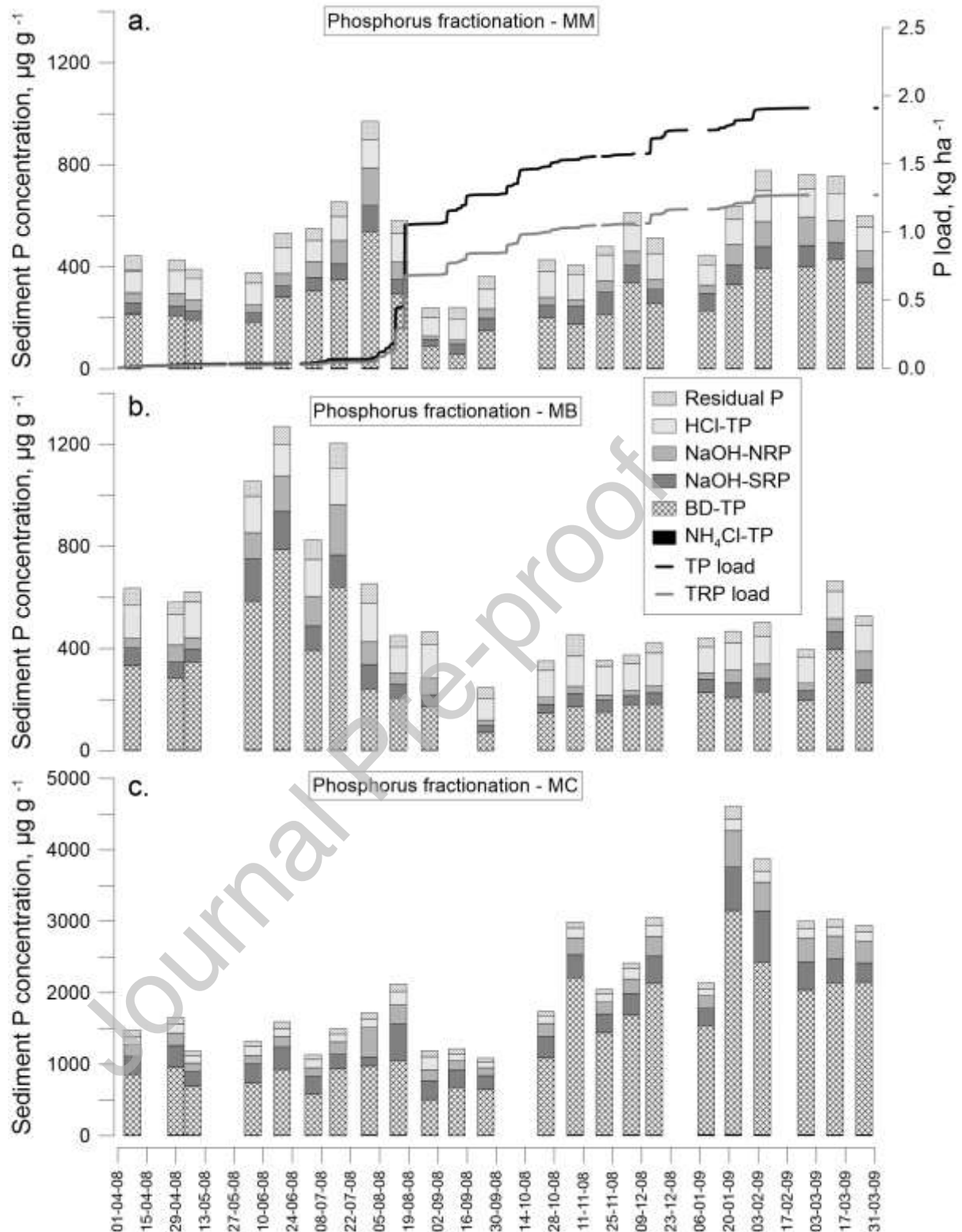


Fig. 8. The development of total and labile to recalcitrant sediment P fractions shown alongside the accumulating P load as measured at the catchment outlets (MM – Fig. 8a) and at upstream sites (MB and MC, Figs. 8b and 8c) in the Co. Monaghan catchment.

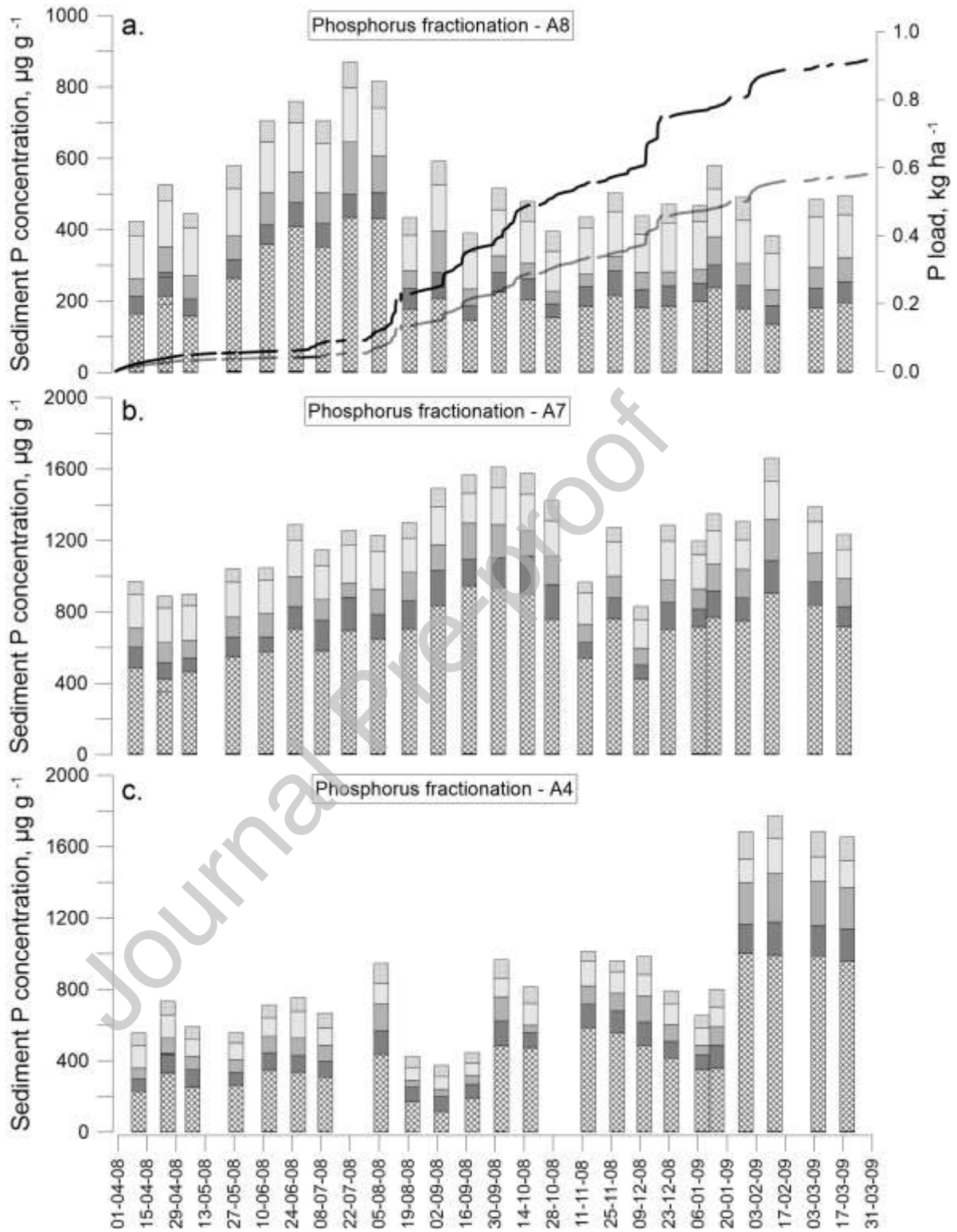


Fig. 9. The development of total and labile to recalcitrant sediment P fractions shown alongside the accumulating P load as measured at the catchment outlet (A8 – Fig. 9a)

and at upstream sites (A7 and A4, Figs. 9b and 9c) in the Co. Armagh catchment. For legend see Fig. 8.

4. Discussion

In this investigation of P in stream bed sediments, under the first objective, sediment TP decreased substantially during the largest storm events, which recovered when base flow re-established. For example, sediment TP concentration at MM, near the Monaghan sub-catchment outlet, fell from a pre-storm level of 971 $\mu\text{g P g}^{-1}$ to 581 $\mu\text{g P g}^{-1}$ after the second largest discharge peak of the study period, and then further down to 240 $\mu\text{g P g}^{-1}$ after the largest storm of the year in August 2008. This is evidence that physical processes were responsible for the bed sediment's net P release and is in-keeping with other studies where hysteresis on rising storm flow has been attributed to stream-bed mobilisation, i.e., sediment and P from a proximal source (Bowes et al., 2005; Jordan et al., 2007; Sherriff et al., 2016).

Sediment P fractionation analysis identified the reductant-soluble BD fraction as the dominant fraction across all six sites: it was the largest in terms of concentration and percentage contribution ratio to sediment TP (median values: 41.1% - 61.9%), with ranges of variation comparable to those of the sediment TP, and the most responsive to change in stream flow. As is expected of the major fraction of sediment TP, BD-TP also decreased rapidly during the August storms. For instance, again at MM, BD-TP concentration fell from a pre-storm level of 534 $\mu\text{g P g}^{-1}$ to 293 $\mu\text{g P g}^{-1}$ (45% reduction) and then to 88 $\mu\text{g P g}^{-1}$ (84% reduction) due to the two largest discharge events in close succession.

The behaviour of the BD fraction in relation to sediment TP and changing stream discharge was also unique in the fact that BD-TP reflected the reduction and recovery in TP not only in concentration terms but also in its contribution ratio terms. In other words, as the sediment TP decreased during storm events, BD-TP decreased disproportionately more than the other fractions, and vice versa, possibly due to increased aeration during disturbance. With the MM site as an illustration, as sediment TP fell and recovered during and after the August storms (971, 581, 240, 242, 363 and 429 $\mu\text{g P g}^{-1}$), BD-TP percentage contribution ratio mirrored that change in sequence (55%, 50%, 37%, 24%, 41% and 46%). This suggests that the BD fraction could be associated with the dominant processes that control sediment P. Furthermore, (not shown here) it has been observed that the Fe/P ratio in the BD fraction fluctuated as the fraction's contribution ratio varied (Fe/P ratios corresponding to the above sequence at MM were: 8.60, 8.26, 17.61, 24.36, 16.35 and 15.16). An important finding here is that this indicates there is a chemical basis to the increase in BD-TP during the recovery from storms - a probable decreasing Fe/P ratio in the BD fraction points to the uptake of P by the reductant-soluble amorphous Fe hydroxide in this fraction (e.g. Jensen et al., 1992; Geurts et al., 2008) – rather than a predominant physical P deposition on the recession of storms.

The comparison between sediment EPC_0 (median values: 0.005 – 0.041 mg P L^{-1}) and stream DRP concentrations (median values: 0.023 – 0.129 mg P L^{-1}), and associations to PEP, suggested that in the majority of cases the bed sediment had potential to retain P from the water column, despite the presence of high labile sediment P concentrations (e.g. Jarvie et al., 2008; Palmer-Felgate et al., 2009). In other words, no evidence was found to show that chemical sediment P release contributed to the

stream water DRP concentration during the stable low flow periods of the summer.

For the second objective and a conceptual model summary, it can be inferred with some confidence that the sediments under study retained P by binding during non-storm periods to a lesser or greater extent in space and time as a legacy store (i.e., Sharpley et al., 2013). This is also likely to mitigate against P enrichment both in the streams and also downstream, as long as the sediment has not been subject to physical disturbance under storm conditions (Simpson et al., 2021). However, this attenuation was dynamic in both time and space as measured by the changing nature of PEP and sediment P fractions, and this adds to the conceptual model on the role of bed sediments for P attenuation. The results also add to the P transfer continuum model of Haygarth et al. (2005), indicating secondary source, mobilisation, and delivery steps. However, it is more difficult to know with confidence what trophic impact would occur when this P-enriched sediment dominated by BD-TP is physically released as an amount of labile P into the river system. For example, the factor that has a decisive influence upon the magnitude of the impact will not necessarily be how much 'dissolved' or 'readily bioavailable' P is going to be released by this mobilised sediment but how long it remains dissolved once disturbed (Rosenberg and Schroth, 2017) and this is likely related to redox conditions in overlying water. The nutrient concentration-trophic state relationship in lotic systems is much less clear than in lakes (e.g., Hilton et al., 2006), because of their own characteristic confounding factors, one of which is indeed flow regime and flooding. Linking the sediment and water P dynamics recorded here with future investigations on the persistence of redox lows through storm events (e.g., Bieroza and Heathwaite, 2015) will be an important consideration. This is a potential next phase in understanding the role of bed

sediments in the eutrophication process of rural streams and rivers.

5. Conclusions

Using synchronous datasets of sediment phosphate exchange potential (PEP), P fractions in stream/ditch sediments and mass P loads from impacted catchments, this study indicated sedimentary P transience in time and space. Gains and losses of P to stream sediments were dynamic and fractionated. PEP was also dynamic in magnitude but rarely reached saturation (and so the potential for chemical P release), despite the presence of high labile sedimentary P fractions. However, these fractions, largely as bicarbonate-dithionite P, were more vulnerable to mass loss during storm events and were more readily re-accumulated following storms with this accumulation likely due to chemical processes. The temporal bioavailability of these labile P losses downstream was identified as a knowledge gap. As ditch sediments were categorised as chemically retaining but physically releasing labile P, their use as linear landscape mitigation features should include such processes in risk assessments.

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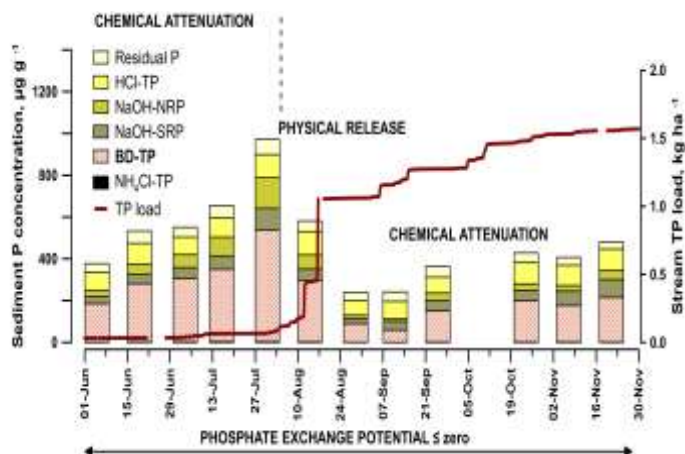
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Graphical abstract



Declaration of interests

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

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

Philip Jordan reports financial support was provided by Special European Union Programmes Body.