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SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES • SHORT ORIGINAL COMMUNICATION

Likely controls on dissolved reactive phosphorus concentrations in baseflow of an agricultural stream

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Abstract

Purpose High baseflow phosphorus (P) concentrations increase the likelihood of periphyton blooms. Several physical and chemical factors can control baseflow P concentrations such as hydraulic exchange with groundwater, particle size-sorting, redox chemistry and different sediment sources. We hypothesized that of these sources, anoxic sediments would allow P-rich groundwater to influence baseflow P concentrations the most and that the measurement of the equilibrium P concentration (EPC_0) of sediments under oxic conditions would not predict P release in anaerobic sediment or baseflow P concentrations.

Materials and methods At four locations along an agricultural stream, we measured dissolved reactive P (DRP), pH, iron, manganese, sulphate, nitrate and dissolved oxygen in streamflow and hyporheic water at 0–200, 200–400 and 400–800 mm depths and P fractions and EPC_0 in sediment samples from the 0–200, 200–400 and 400–800 mm depths.

Results and discussion Concentrations of DRP in streamflow and shallow hyporheic zone water increased downstream and were mirrored by concentrations in shallow sediment, EPC_0 measurements of oxic sediments and deeper hyporheic waters. Groundwater samples and the EPC_0 in deeper sediments did not show a pattern or residence time consistent with the supply of P to baseflow despite deeper sediment being anoxic and less likely to sorb upwelling P. There was also no change in pH or particle size downstream ruling out the degassing of groundwater or sediment size-sorting as an influence. However, the composition of sediment and underlying lithology of the catchment pointed to sediment downstream that was different to upstream sediment in that it could store and release more P.

Conclusions Given the strong influence of sediment source on baseflow P concentrations, efforts to decrease the likelihood of periphyton blooms under baseflow should focus on reducing the erosion of P-rich sediment. Furthermore, the presence of oxic conditions in surface sediment meant that there was a relationship between EPC_0 and hyporheic water P concentrations. However, mixed oxic/anoxic conditions in deeper layer may require EPC_0, or release rates, to be measured under reducing conditions.

Keywords Anaerobic · Hyporheic zone · Groundwater · Lithology · Runoff · Sediment/water interactions

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1 Introduction

The enrichment of streams with phosphorus (P) can impair water quality by enhancing the growth of periphyton blooms under baseflow conditions. Inputs of P during baseflow in agricultural catchments can come from wastewater, the dung of grazing animals, fertilizer, bed sediments or groundwater (Rogers et al. 2012). However, fencing-off streams from animals effectively mitigates the direct input of P-rich dung (Hughes and Quinn 2014). Similarly, efforts to decrease P inputs by treating wastewater have proven to be successful in many cases (Romero et al. 2016).

In addition to fencing and wastewater treatment, research from the 1970s focused on the supply of P by bed sediments (Taylor and Kunishi 1971). The supply of P has been characterized as a function of sediment size and sediment composition. For instance, although coarser sediments may not contain as much P as fine sediments, under oxic conditions, they are thought to release more P per unit mass into the water column due to a combination of lower sorption and easier exchange with interstitial water (Stone et al. 1995). The amount of P available for exchange is influenced by sediment composition, which is influenced by floods that can remove or introduce new sediment of different soil types and land use (Palmer-Felgate et al. 2009). However, more recently, evidence has surfaced of the increasing importance of anaerobic conditions that solubilize P from iron (Fe) oxides (Parsons et al. 2017), the smothering of the stream bed by fines which lead to limited exchange and uptake of P by deeper sediments (Weigelhofer et al. 2018) and the solubilization of P due to increasing pH from degassing Ca-rich groundwater (McDonald et al. 2019).

The enrichment of groundwater with P has been noted in many areas with intensive agriculture (Holman et al. 2008). However, local conditions such as long transit times and reducing conditions may also enrich P to the point where it mirrors surface water concentrations (Holman et al. 2010). Under hypoxic (or even anoxic) conditions, P is released from the sediment resulting in the possibility that upwelling groundwater could contribute significantly to baseflow concentrations of P (Kjaergaard et al. 2012; Gu et al. 2019). Some studies have shown a link between shallow groundwater P concentrations in headwater catchments and baseflow P concentrations (Mellander et al. 2016). Correlations between the change in baseflow and groundwater P concentrations have also been made at sites across countries, although the influence of site-specific reducing conditions, relative to other factors such as land use and aquifer composition, was unclear (McDowell et al. 2015). Additional research on bed sediment and groundwater inputs is required to isolate and manage the controlling factors to efficiently and effectively decrease baseflow P concentrations and the likelihood of periphyton blooms.

The control and management of baseflow P by sediment has been investigated widely by the measurement of the equilibrium P concentration at zero net sorption or desorption (EPC_0) (Agudelo et al. 2011; Palmer-Felgate et al. 2011; Weigelhofer et al. 2018). In assessing soil and streamflow P concentrations, Brennan et al. (2017) used the EPC_0 as an indicator of likely periphyton growth. Others have used EPC_0 to indicate the buffering capacity and the likely lag time between stopping a point source discharge to the stream and the decrease of stream dissolved reactive P (DRP) concentrations to desired levels (Haggard and Stoner 2009). However, Palmer-Felgate et al. (2011) noted that the ability of the EPC_0 to predict DRP in a wetland sediment was inferior to that of a diffusive equilibrium thin film, and hypothesized that this was due to reducing conditions that could not be replicated ex situ. Where there is good exchange between the hyporheic zone and the water column, the presence of reducing conditions in the hyporheic zone could therefore impair our ability to use EPC_0 to forecast the risk of periphyton blooms under baseflow and the response of a stream to catchment actions.

We used a well-studied catchment in the North Island of New Zealand to gather data on the composition of sediment, stream water, hyporheic pore water at different depths and groundwater. Our primary hypothesis was that reducing conditions in subsurface sediments would allow P-rich groundwater to influence baseflow P concentrations. Our secondary hypothesis was that the measurement of EPC_0 under oxic conditions is not a useful indicator of P release in anaerobic sediment and therefore cannot be used to predict baseflow P concentrations.

2 Materials and methods

2.1 Site characteristics and sampling

The study was conducted in the Kopuhurihuri (9.1 km^2) catchment, nestled within the Waiotapu Stream and the Reporoa Basin of the North Island of New Zealand (Fig. 1). Elevation in the catchment ranges from about 500 m ASL (above sea level) along the ridgelines to about 300 m ASL at the catchment outlet. Mean annual temperature is 12.6 °C. Rainfall averages 1267 mm and is distributed evenly throughout the year (Piper 2005). Soils are dominated by organic matter-rich (> 10% carbon, C) Taupo sandy loams (New Zealand Soil Classification, Orthic Pumice soil; USDA Taxonomy, Typic Udivitrand (Hewitt 2010). Streams are deeply incised with the stream bed often 2–4-m below the topsoil. The major rock types in the catchment are mapped as a combination of non-welded ignimbrite from the 181 AD Taupo eruption, middle Pleistocene rhyolite 0.128–0.524 million years old and late Pleistocene river deposits 0.012–0.027 million years old (Edbrooke et al. 2014). Land use is dominated by intensive dairying supported by moderate application rates of nitrogen (N) and P fertilizer (~ 200 kg N ha^{-1} yr^{-1} and 38 kg P ha^{-1} yr^{-1}, respectively). Plantation forestry (*Pinus radiata* sp.) occurs in the higher elevations (> 400-m ASL) along the eastern catchment boundary.

Samples of sediment, stream water and hyporheic water were taken at four locations along the Kopuhurihuri Stream in March 2018. These were labelled K1, K3, K4 and K5 as per McDowell et al. (2019). Sites were chosen to represent two sites of modest flow (K4 and K5) fed by the headwater springs and two sites near the outlet (K1 and K3) with considerably

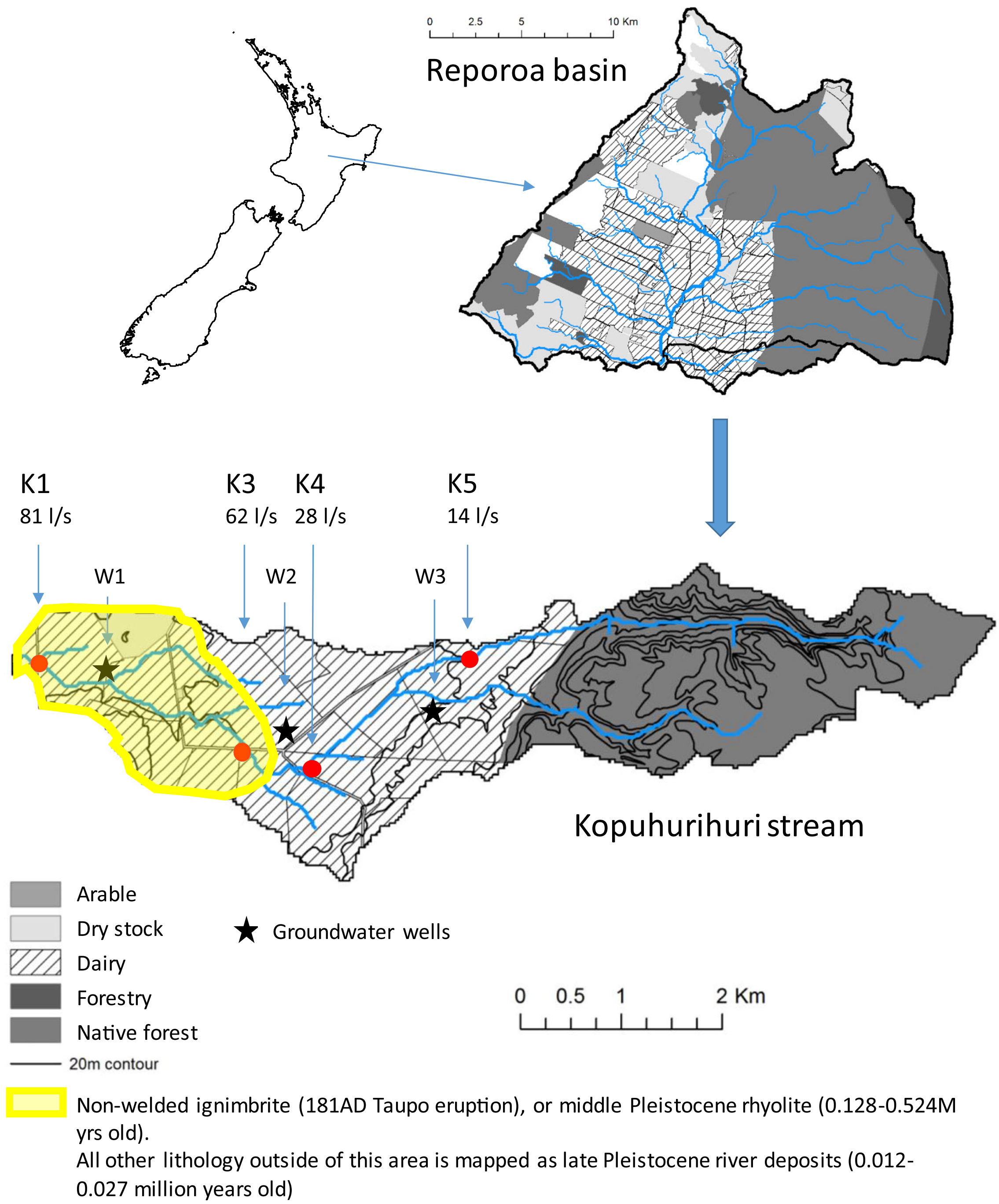

Fig. 1 Map showing land use, contours, example flow rates and the relative location of sediment sampling sites (K1, K3, K4, K5) and groundwater well (W3–W8) within the Kopuhurihuri Stream catchment

more flow likely fed by deeper and older groundwater flowing through different geology (Fig. 1).

Although flow was not continuously measured in the Kopuhurihuri Stream, a continuous record was available *c* 1 km downstream of the confluence of the Kopuhurihuri and the larger Waiotapu Stream site since 1962. Streamflow in the Waiotapu Stream catchment is relatively stable with chemistry-assisted hydrograph separation suggesting on average 64% is slow flow (deep groundwater), 24% is medium flow (shallow groundwater), and 13% is fast flow (near-surface pathways) (Woodward and Stenger 2018); modelling by Piper (2005) suggested that stormflow in the Kopuhurihuri Stream is, on average, 7% of total flow. Sampling occurred during a sustained period of baseflow in the Waiotapu Stream and therefore Kopuhurihuri Stream. Median daily flow in the Waiotapu Stream over the preceding 3 months was 3.7 $m^3\ s^{-1}$, and the 75th percentile of flow was 4.1 $m^3\ s^{-1}$, compared with the annual median flow and 75th percentile of 4.4 and 4.8 $m^3\ s^{-1}$, respectively.

At each site, samples of sediment (0.2 kg wet weight) were taken either by a shovel of the top 2 cm or a 5 cm diameter corer of the 20–40 and 40–80 cm depths from five locations at each site. Each site was uniform devoid of riffles or pools that could unduly influence sediment composition. The top 20 cm was typically unconsolidated and difficult to sample intact by corer, and consequently, we did not collect the 2–20 cm depth. Sediment samples were weighed and wet-sieved in the field through a 4 mm sieve. The < 4 mm fraction was weighed and kept cool (4 °C) during transport back to the laboratory. We chose to use a larger particle size cut-off than the normal < 2 mm to include potential P sorption by large particles (Clarendon et al. 2019) while still obtaining a sample that could be homogenized and weighed in the lab without generating a bias towards any particle size.

Stream and hyporheic water samples were taken at 9 am, 11 am, 2 pm and 4 pm at each site. These were analysed separately but treated as replicates since previous work at these sites identified no diurnal trends relevant to our study (McDowell et al. 2019). Dissolved oxygen, pH and temperature were also assessed during sampling. Hyporheic samplers consisted of a 2.5 cm diameter clear plastic tube with an aluminium (Al) rod inserted through the centre. With the rods inserted, tubes were pushed to 20, 40 and 80 cm into the bed, leaving approximately 0.5 m above the water line. There were three samplers at each site. The three tubes for each depth were grouped in an array across the channel with each tube spaced approximately 0.5 m apart. The 80 cm array was 5 m downstream of the 40 cm array, which was 5 m downstream of the 20 cm array. This arrangement avoided shallower arrays being influenced by the sampling of upwelling hyporheic water in deeper arrays. Before sampling, the rod was removed, and the void space was allowed to fill with hyporheic water from the 20, 40 and 80 mm depths. This water was removed five times over 3 min by a syringe with attached plastic tubing, before the hyporheic sample was taken. Rapid infilling of the sampler was an indication of strong upwelling and free exchange from sediment at each depth (Ward et al. 2012), although we did not specifically measure the vertical hydraulic gradient. Stream and hyporheic water samples were bulked together within a site and depth, yielding 64 samples, 4 sites by 4 depths (including stream water) and 4 replicates over time. All bulked water samples were filtered (< 0.45 μm) in the field and split in two with one of the samples acidified with 0.5 mL of 1 M HNO_3 to prevent precipitation of iron (Fe) and manganese (Mn).

In an associated study (Clague et al. 2019), DRP concentration depth profiles in shallow groundwater were measured (but unpublished) in autumn 2016 at six well sites, spread across three neighbouring dairy farms (W3/W4 = downstream, W5/W6 = mid-point and W7/W8 = upstream, see Fig. 1). A packer system allowed samples to be taken from specific depths, from near the groundwater table to approximately 3 m below the water table. Samples were treated and analysed for the same set of analytes as per the hyporheic samples. Tritium-derived mean residence time was sourced from Clague et al. (2019).

2.2 Water and sediment analyses

In the laboratory, filtered water samples were analysed for DRP, nitrate-N, ammonium-N and sulphate using standard APHA methods (APHA-AWWA-WEF 2005). The filtered and acidified water samples were analysed for iron (Fe), manganese (Mn) and calcium (Ca) via inductively coupled plasma optical emission spectrometry (ICP-OES). Concentrations of nitrate-N, sulphate, Mn and Fe were used to calculate the potential redox status of surface water and hyporheic samples using the method of McMahon and Chapelle (2008).

A 100-g subsample of sediment was oven dried (40 °C) to determine moisture content. Oven-dried sediment was used to determine the percentage of sand (> 63 μm) and fines (< 63 μm) by the hydrometer method (Gee and Bauder 1986) as well as pH in water (Hendershot et al. 1993), organic C and nitrogen (N) by LECO C/N analyser and anion storage capacity (ASC), which measures Al and Fe concentration (Saunders 1965). A subsample was also subjected to a Kjeldahl digestion (Taylor 2000), and total Al, Ca, Fe, Mg and Mn determined via ICP-OES.

Refrigerated, wet sediment samples were used for P sorption-desorption experiments yielding EPC_0 and P fractionation. All P analyses used the colorimetric method of Watanabe and Olsen (1965). Previous work by Lucci et al. (2010) showed that measurements examining the sorption-desorption of P from sediments were sensitive to stream water chemistry. Hence, a synthetic river water solution containing 0.002 M $CaCO_3$ and 0.0001 M NaCl and 0.0001 M $MgSO_4$ was used representing the median ionic strength and Ca, sodium (Na), chloride, carbonate and sulphate concentrations of 76 New Zealand rivers (McDowell 2015). This solution was mixed with P (as KH_2PO_4) to make solutions containing 0, 0.1, 0.25, 0.5, 2.5, 10 and 30 mg P mL^{-1}. Whole wet sediments (equivalent of 1-g dry weight) were mixed with 20 mL of the above solutions and shaken for 16 h. Samples were then filtered (< 0.45 μm), and was determined. The Langmuir equation was fitted to a plot of P sorption (y-axis) against P in solution (x-axis). The EPC_0 was determined as the estimated concentration at which no net sorption or desorption occurred on the x-axis. The standard error of the fit of the Langmuir equation to the data was used to determine an average limit for detecting the EPC_0 at 0.004 mg P L^{-1}.

Phosphorus fractionation on fresh sediments was started within a week of sampling using the scheme of Jan et al.

(2015). Triplicate samples of 0.5 g dry weight equivalent sediment were sequentially extracted by shaking the sediment end-over-end with 30 mL of deionized water (H_2O-P), then two sequential extractions (BD-1 and BD-2) with 10 mL of bicarbonate-dithionite (0.1 M $NaHCO_3$ and 0.1 M $Na_2S_2O_4$, pH 7.2), followed by two sequential extractions (NaOH-1 and NaOH-2) with 1 M NaOH and, finally, a single extraction with 1 M HCl (HCl-P). A 0.5 M NaCl wash step was included after the BD-2 and NaOH-2 steps to prevent carryover to the following fraction. After shaking, samples were centrifuged (10 min at 2400×*g*) and filtered (Whatman grade 41) before the next extract or wash was included. The H_2O, BD and NaOH fractions were shaken for 30 min, while the HCl fraction was shaken 16 h. The sediment was then dried and digested via a Kjeldhal digestion (Taylor 2000), and remaining P was defined as residual P. The sum of all fractions represented the total P concentration in the whole sediment. Extracted fractions of sediment P represented labile or loosely bound P (H_2O-P); P bound to less-crystalline and surface-active Fe (hydro) oxides (BD-1); P bound to poorly active and crystalline Fe (hydro)oxides (BD-2); P bound to active Al (hydr)oxides, labile organic matter or clay minerals (NaOH-1); P bound to crystalline Al (hydr) oxides, refractory organic matter or clay minerals (NaOH-2); and primary Ca-P minerals (HCl-P).

We analysed all extracts for P using ICP-OES, yielding total P in the extract. We did not distinguish between inorganic or organic P in the BD and NaOH extracts since BD is known to extract little organic P (Jan et al. 2015), while previous work on these sediments showed that organic P represented < 10% of P extracted by NaOH (McDowell et al. 2019).

All data was tested for normality and log-transformed (if not normally distributed) before statistical analysis using Genstat v17 (Genstat Committee 2015).

3 Results and discussion

The mean physical and chemical characteristics of sediments are given in Table 1, while the corresponding stream water and hyporheic water DRP concentrations and pH are given in Fig. 2. The sediment data show a decrease in ASC, organic C, H_2O-P, BD1-P and total P with depth across all sites, while some sites exhibited decreases in less reactive P fractions (BD2-P, NaOH1 and 2 P, HCl-P and residual P) and sand content. Whereas sand content decreased and silt content increased with depth, no consistent changes with depth were noted for clay content or pH nor between sites at the same depth for particle size, pH, ASC or organic C; however, like at previous samplings of the Kopuhurihuri Stream (McDowell et al. 2019), concentrations of P in different sediment fractions, especially the reactive fractions (H_2O-P and BD1-P), tended to increase downstream.

Stream water DRP concentrations increased downstream from 0.013 (K5) to 0.032 mg L^{-1} (K1) and for the two downstream sites (K1 and K3) from 0.022 to 0.094 mg L^{-1} with depth in hyporheic samples (Fig. 2). There was some similarity between changes in the concentrations of different sediment P fractions, total P and the concentrations of DRP in streamflow or in hyporheic samples. There are several factors that could be responsible for this similarity. For instance, sediment P could change in response to (1) physical processes such as hydraulic exchange and particle size-sorting (Stone et al. 1995), (2) the chemical composition of sediment deposited via erosion and runoff onto the streambed from different sources downstream (Shore et al. 2016) and (3) sediment chemistry in the hyporheic zone and the upwelling of P-rich groundwater (McDonald et al. 2019). We examine each factor individually with the aim of discerning the main factor controlling streamflow P concentrations at baseflow.

3.1 Physical processes

Storm events can lead to a change in the particle size and P concentration of bed sediments by scouring and depositing sediment. Weigelhofer et al. (2018) noted that the deposition and build-up of fine sediment (< 2 mm, averaging 54% across 11 streams) restricted the exchange of P between deeper sediments and the water column. These authors attributed this restriction as a likely cause of the poor relationship between surface sediment EPC_0 and stream water DRP concentration. However, the volcanic rocks and soils in the wider Waiotapu catchment tend to be freely draining and have an abundance of coarse-sized particles (Piper 2005). Similarly, our data showed that the particle size distribution of the Kopuhurihuri Stream sediments was much coarser (clay-sized particles comprised on average 4% of sediment) than in the study of Weigelhofer et al. (2018), suggesting good exchange between the sediment and water column (Table 1).

Sediment size-sorting can alter the concentration of P in sediments and the likely desorption of P into the water column. Coarser particles tend to contain less P per unit mass but desorb it more readily than finer particles (Stone et al. 1995). However, the proportion of sand, silt and clay in surface sediments did not vary down the catchment, indicating that size-sorting was not likely to be a factor influencing P dynamics.

3.2 The likely source of sediment and its chemical characteristics

The origin of sediments influences the quantity and distribution of P in different chemical pools and the likelihood of these pools releasing P to the water column (Shore et al. 2016). Land use in the Kopuhurihuri Stream is either production forestry in the headwaters or dairying everywhere else. The erosion of sediment and resulting streamflow sediment loads

Table 1 Mean chemical concentrations and particle size determination of sediment samples from triplicate analyses of samples taken at each site up the catchment, beginning with the most downstream site, K1

Site	Depth[1] (cm)	ASC[2] (%)	pH	Org. C (g kg^{-1})	H_2O-P (mg kg^{-1})	BD1-P (mg kg^{-1})	BD2-P (mg kg^{-1})	NaOH1-P (mg kg^{-1})	NaOH2-P (mg kg^{-1})	HCl-P (mg kg^{-1})	Residual P (mg kg^{-1})	Total P (mg kg^{-1})	Sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})
K1	Surface	48	6.8	6.6	5.6	309	132	66	29	77	193	812	887	111	2
K1	20–40														
K1	400–80	19	5.4	3.8	0.3	59	20	31	18	115	39	283	854	144	2
K3	Surface	38	6.7	4.6	2.4	131	52	50	18	110	181	544	931	69	0
K3	20–40	22	7.6	2.4	0.7	29	10	28	15	139	199	421	897	101	2
K3	40–80	20	6.3	1.2	0.4	11	6	12	23	6	49	108	675	317	8
K4	Surface	53	6.1	8.5	4.9	141	77	89	39	109	37	497	858	138	3
K4	20–40	26	7.0	2.2	1.0	54	21	23	11	127	7	245	782	216	3
K4	40–80	16	7.4	0.9	0.5	5	2	10	6	87	8	117	705	290	5
K5	Surface	25	6.1	6.2	2.2	95	16	26	13	133	34	317	952	48	0
K5	20–40	29	6.4	6.3	0.5	46	19	28	13	82	8	197	902	97	1
K5	40–80	15	7.2	2.5	0.6	5	2	13	10	94	15	140	684	309	7
LSD		14	1.0	4.6	1.0	75	51	20	12	22	114	152	105	112	3

[1] 'Surface' denotes the upper 2 cm of stream bed sediment; samples of the 20–40 cm depth at K1 were not able to be obtained

[2] Anion storage capacity

LSD is the least significant difference at the $P < 0.05$ level to compare site by depth means

for mature forestry and dairying are low, averaging 317 and 299 kg ha^{-1} yr^{-1}, respectively, across New Zealand (McDowell and Wilcock 2008; Baillie and Neary 2015). However, P losses and resulting P concentrations in streams draining dairying can be 2–3 times greater than streams draining production forestry (Baillie and Neary 2015). These greater losses can be caused by factors such as (1) the greater application of P to land as fertilizer or farm dairy effluent (Monaghan et al. 2007), (2) more P transport in surface runoff or subsurface flow caused by lower evapotranspiration in pasture compared WITH trees (Hughes and Quinn 2014) and (3) the grazing of stock which disturbs the soil or destabilizes stream banks in areas where cows are not excluded from stream margins (Wilcock et al. 2013). Although dairying surrounded all sites, it is plausible that the signature of forest-derived sediment and P decreased quickly towards our most downstream sampling site.

Additional clues to the origin of sediment at the two downstream sites are given in Table 2 in the form of major element concentrations in sediments and in Fig. 1 showing the underlying lithology of the catchment. Data for lithology of the Kopuhurihuri catchment helps map the likely rock type at the two downstream sites as either non-welded ignimbrite and reworked deposits from the 181 AD Taupo eruption or middle Pleistocene rhyolite (0.128–0.524 million years old), whereas the lithology at the upstream sites was mapped as late Pleistocene river deposits (0.012–0.027 million years old) (Edbrooke et al. 2014). Although insufficient data were available to use techniques such as sediment fingerprinting (Walling 2013) to more accurately determine the origin of sediment, Lowe et al. (2008) found that concentrations of major elements such as Fe and Mn were enriched in rhyolite of the Taupo eruption, whereas the Fe and Mn concentrations of sands and silts tended to be less. In general, Fe and Mn concentrations were greater at the downstream sites (15,454 mg Fe kg^{-1} and 327 mg Mn kg^{-1}) than those at the upstream sites (7305 mg Fe kg^{-1} and 105 mg Mn kg^{-1}), suggesting sediment that were of different lithological origin.

Further investigation of sediment at each site shows large differences in the concentration of different P fractions (Table 1). These differences support the presence of volcanic-derived rocks and sediment downstream. Among P fractions, most P was stored in BD fractions, which increased with distance downstream and decreased with depth. These fractions are indicative of P bound to less crystalline and surface-active Fe (hydro)oxides (BD-1) and P bound to poorly active and crystalline Fe (hydro)oxides (BD-2) (Jan et al. 2015). Such compounds are more common in volcanic-derived rocks and sediment than those derived from alluvium or marine deposits (McDowell 2015). In contrast, HCl-P showed few differences downstream or with depth. The HCl-P fraction is thought to extract Ca-P minerals like

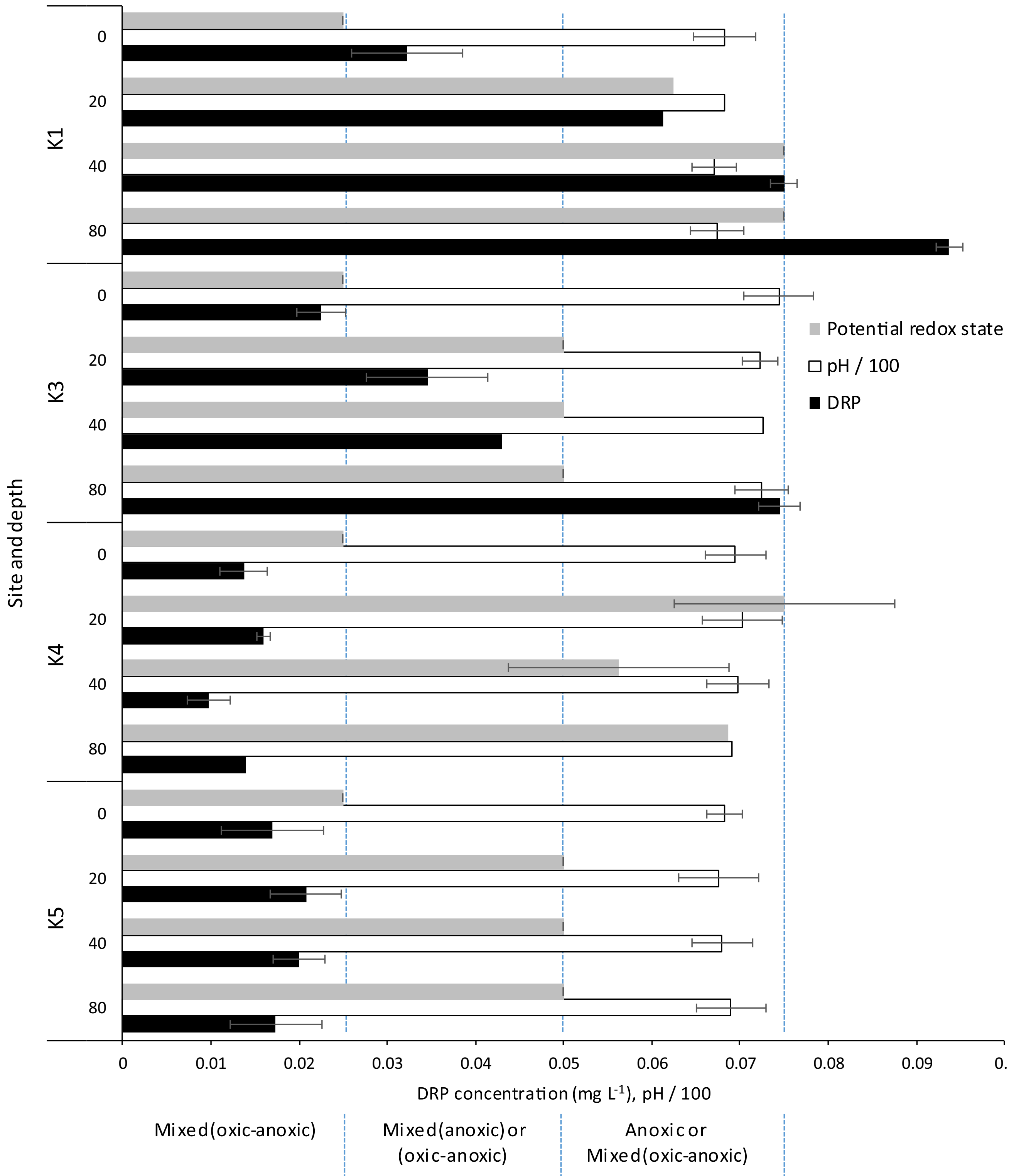

Fig. 2 Mean dissolved reactive P concentration, pH and potential redox state calculated using the method of McMahon and Chapelle (2008) in the hyporheic water samples at three depths (200, 400 and 800 mm) and overlying stream water (labelled depth = 0) for each site in the Kopuhurihuri Stream. The most downstream site is K1. Error bars represent the 95% confidence intervals calculated from the replicates in space and time at each site

hydroxyapatite and is not sensitive to changes in redox status (Jan et al. 2015). Rhyolite and associated ignimbrite within the wider Taupo Volcanic Zone are known to have few Ca-containing minerals (Ewart 1965).

The decrease of BD-P concentrations with depth could be due to the dissolution of Fe (hydro)oxides and P under reducing conditions (Parsons et al. 2017). However, if reducing conditions occur, the capacity of Fe and Mn oxides to sorb P is impaired, thereby opening the possibility that groundwater could be a source of P to stream flow.

3.3 Sediment chemistry and the upwelling of groundwater

If sediment P-sorption capacity was impaired by reducing conditions and groundwater was the sole or controlling factor of DRP concentrations in surface waters, there should be little difference between surface water DRP concentrations and concentrations in groundwater, hyporheic samples or measurements of EPC_0. However, it is also possible that uptake by biota may have influenced P during upwelling, although other data has found similar rates of microbial processing in hyporheic zone and surface sediment (Burrows et al. 2017).

In contrast to the stream water, there was no apparent increase in groundwater concentrations down the catchment. Overall, the range of DRP concentrations in groundwater (Fig. 3) was like that measured in surface water (Fig. 2), but some variation was noted at specific sites. For instance, well sites W4, W5 and W8 had lesser concentrations than observed in surface water, while sites W3, W6 and W7 had similar or greater concentrations. There are a few plausible reasons for this, such as the ability of a few groundwater samples in six wells to represent spatial or temporal variation in streamflow, that the sampled groundwater was not connected to the stream at baseflow or that sediment chemistry was controlling P concentrations.

Marked temporal variation was observed at some sites. Associated estimates of tritium-derived mean residence time (MRT) (Clague et al. 2019) showed that water sampled at the upstream well was likely to be much older than that in the middle or downstream wells (Fig. 3). The high MRT, despite the shallow sampling depths (Fig. 3), indicated that some of the sampled groundwater was effectively not connected to surface water and therefore not contributing substantially to baseflow, for example, in the deepest samples from the upstream wells (W7, W8) and the deepest sample at the mid-point well W6, which may be below an aquitard (Clague et al. 2019). However, some sites indicated that the groundwater was well connected to the stream because of low-MRT groundwater. These were sites at the mid-point (W5) and downstream (W4), both exhibiting low DRP concentrations (< 0.002 mg L^{-1}), and at a shallow depth at W6 which had a DRP concentration like stream water (~ 0.03 mg L^{-1}). The observed spatial and temporal variability in groundwater DRP and MRT makes it difficult to conclude whether groundwater inputs are contributing and are responsible for the increasing stream water DRP concentrations down the catchment.

Hyporheic-DRP concentrations were enriched at downstream sites K1 and K3 compared with K4 and K5 (Fig. 2). Concentrations were also enriched in deeper layers in the K1 and K3 sites (≥ 0.07 mg L^{-1}) compared with surface waters. This is good evidence for surface sediment influence or control on the relative change in DRP concentrations downstream and for the enrichment of DRP due to reducing conditions at depth (i.e. under likely anoxic or mixed anoxic-oxic conditions, Fig. 2) (Hupfer and Lewandowski 2008). There was a marked difference in dissolved oxygen concentrations in the shallow (0–20 cm depth) hyporheic samples (mean = 2.05 mg L^{-1}) compared with

Table 2 Mean chemical concentrations and particle size determination of ediment from triplicate analyses of samples taken at each site up the catchment, beginning with the most downstream site, K1

Site	Depth[1] (cm)	Aluminium (mg kg^{-1})	Calcium (mg kg^{-1})	Iron (mg kg^{-1})	Magnesium (mg kg^{-1})	Manganese (mg kg^{-1})
K1	Surface	6085	1849	19,042	591	316
K1	20–40					
K1	40–80	4726	1786	10,424	718	339
K3	Surface	4135	1206	18,133	783	369
K3	20–40	9400	1573	13,028	615	368
K3	40–80	5631	738	20,230	734	241
K4	Surface	4117	1679	16,555	476	351
K4	20–40	3006	1067	6437	356	66
K4	40–80	2614	735	2326	248	27
K5	Surface	5083	1331	9672	638	85
K5	20–40	4795	1035	6572	460	73
K5	40–80	3060	729	2273	307	32
LSD		1109	257	3734	230	83

[1] Samples of the 20–40 cm depth at K1 were not able to be obtained

LSD is the least significant difference at the $P < 0.05$ level to compare site by depth means those below 20 cm (mean = 0.47 mg L^{-1}). Gu et al. (2019) hypothesized that reducing conditions or an increase in pH was likely to cause an increase in DRP release from sediment. They found that DRP release in sediments with high extractable P and low organic matter concentrations was likely controlled by the reductive dissolution of Fe-oxyhydroxides. Such conditions were observed in the subsurface sediments of the Kopuhurihuri Stream.

Other research showed that pH and DRP concentrations increase as CO_2 degasses from groundwater-fed baseflow (McDonald et al. 2019). However, pH measurements in streamflow and at depth showed no change (i.e. all pH values were between 7 and 7.3). We therefore conclude that although reducing conditions will have induced P release (Kjaergaard et al. 2012) and impaired the sorption of P from upwelling groundwater, the oxic status of surface sediments was sufficient to buffer greater P concentrations from deeper layers.

3.4 The use of EPC_0 to indicate likely P concentrations in baseflow and at depth

If we assume that hyporheic water samples were in equilibrium with oxic sediment, the concentration and relationship between EPC_0 and hyporheic water samples should be similar. A relationship was present between DRP in baseflow and the EPC_0 of the top 2 cm of surficial sediment (Fig. 4). However, no such relationship was found between hyporheic DRP and EPC_0 at deeper depths. This would suggest that the observed mixed oxic/anoxic conditions mean that the equilibrium measurement under standard oxic conditions is less able to explain P dynamics in subsurface sediments (see also Fig. 5). Under anaerobic conditions, sediment Fe and Mn will be soluble leaving P release to be a function of calcium-bound P and organic P decomposition (Hupfer and Lewandowski 2008). However, soluble Fe and Mn will have likely precipitated under oxic conditions in the lab thereby boosting P sorption and decreasing EPC_0 (Simpson et al. 2019). This agrees with work by Palmer-Felgate et al. (2011) who found a poor relationship between EPC_0 and DRP in an anoxic wetland sediment.

It is also possible that the discrepancy between DRP and EPC_0 could be caused by a different rate of release of P into the hyporheic samples at depth than at the sediment surface. The kinetics of release have been found to be a function of hyporheic exchange and sediment size, usually serving as a

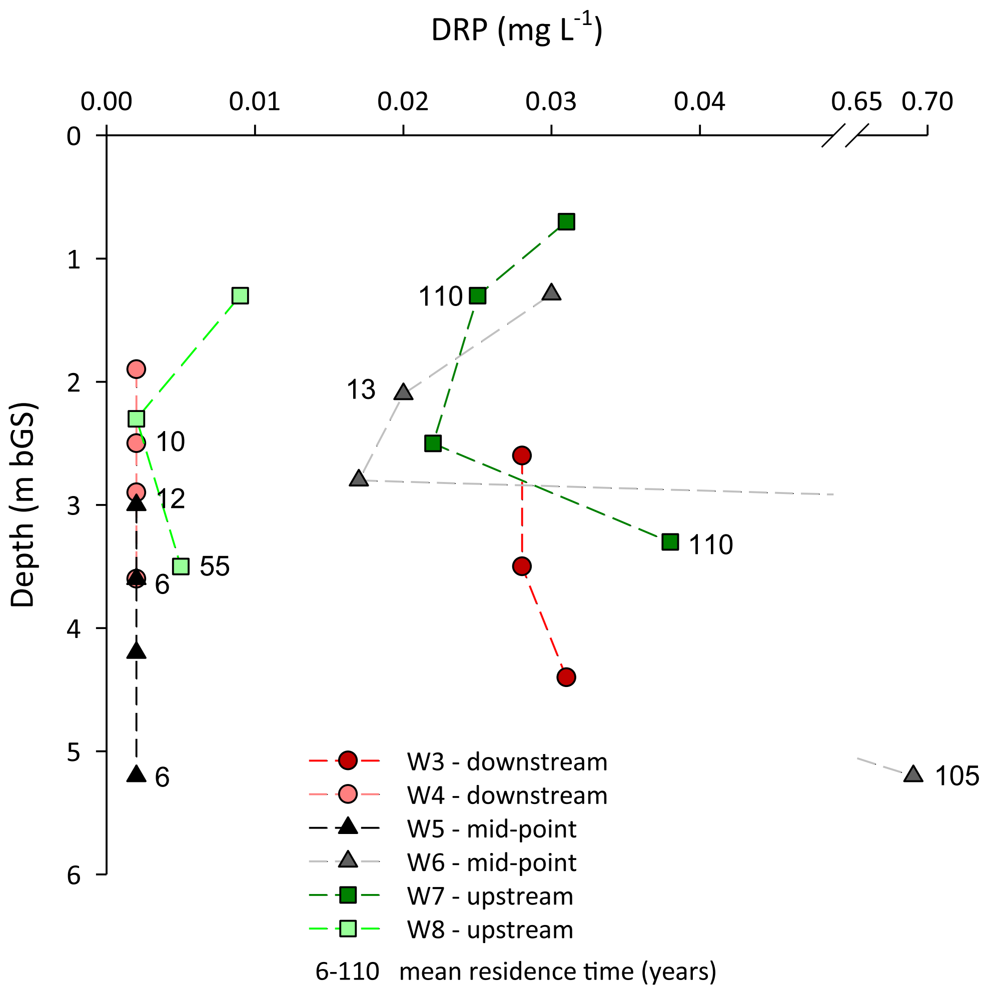

Fig. 3 Vertical profiles of groundwater dissolved reactive P (DRP) concentrations as point data and the mean residence time (MRT) in text at six groundwater monitoring sites in the Kopuhurihuri Stream catchment. Data for MRT was sourced from Clague et al. (2019)

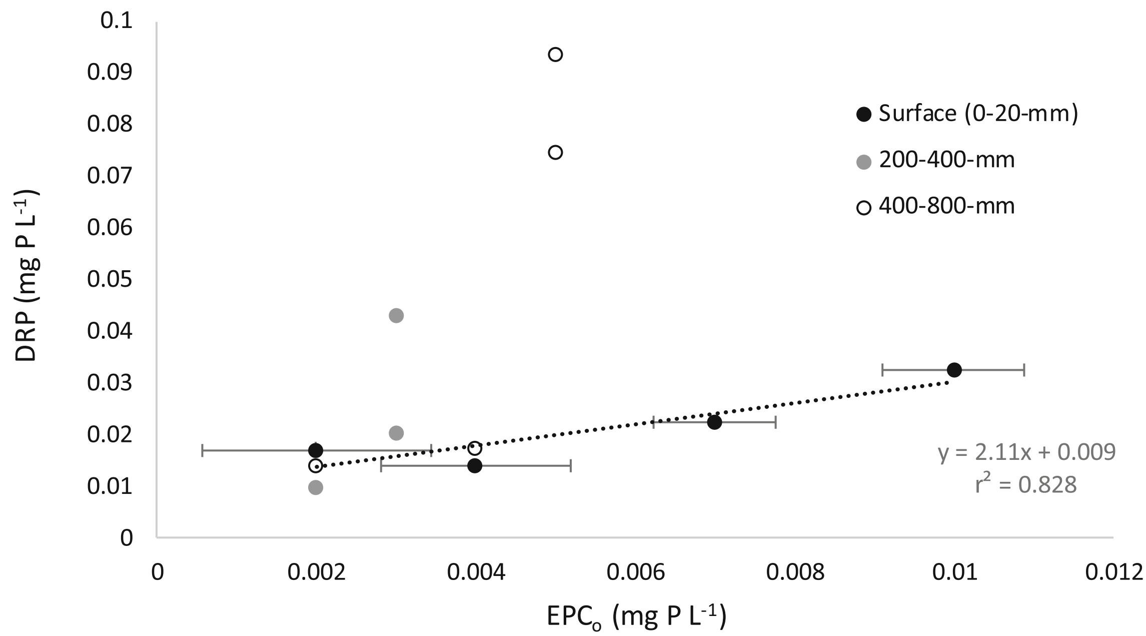

Fig. 4 Plot showing the concentration of dissolved reactive P (DRP) in hyporheic water samples and the equilibrium P concentration at zero net sorption or desorption (EPC_0) for different sediment depths. The line shows the significant ($P < 0.05$) fit between DRP and EPC_0 for the surface sediment. Error bars represent the 95% confidence intervals calculated from replicates in space and time at each site

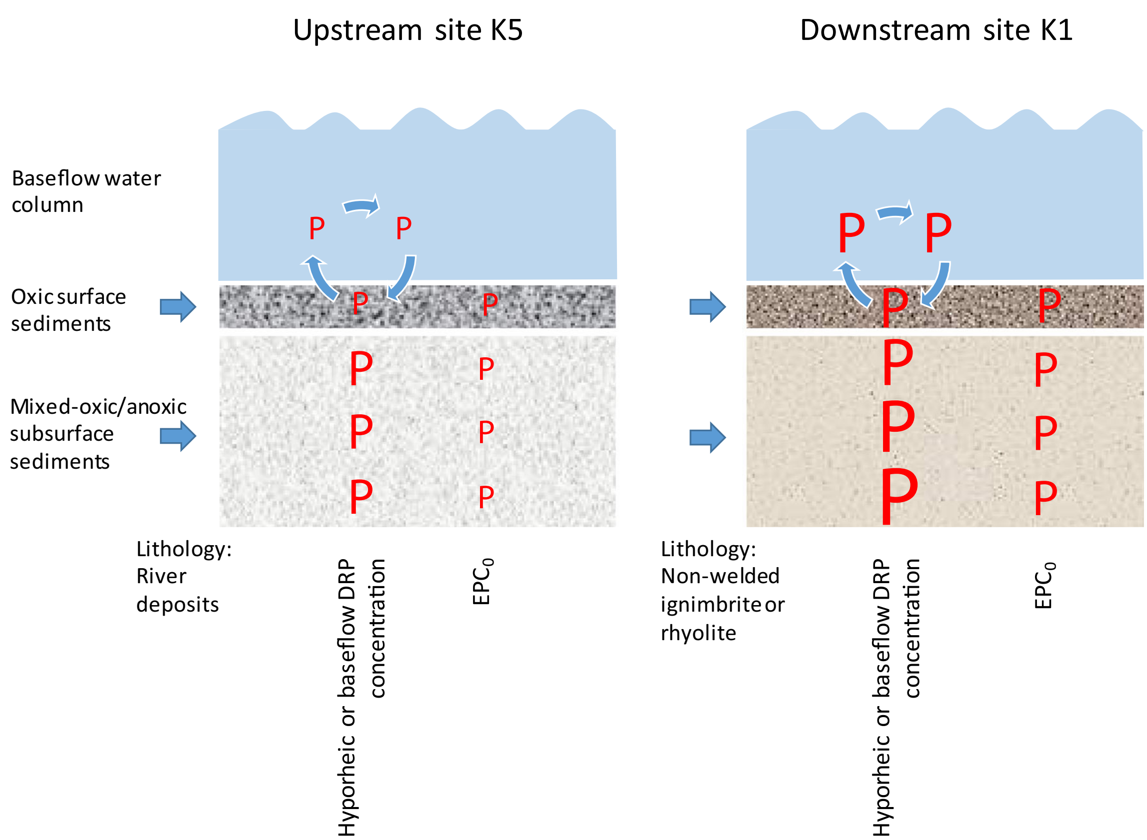

Fig. 5 Schematic representation showing the concentration of P in the hyporheic zone or baseflow as measured or predicted by the equilibrium P concentration at zero net sorption or desorption (EPC_0) for the oxic surface and mixed oxic/anoxic subsurface sediment at an upstream and downstream site with sediment likely sourced from different lithology. The size of the P indicates the relative magnitude of P concentrations

proxy for the number and accessibility of P sorption sites (Clarendon et al. 2019). While we cannot discount variable rates of upwelling and P exchange, particle size did not vary with depth and can be discounted as a factor (Table 1). We therefore hypothesize that to generate a good relationship between EPC_0 and DRP in hyporheic water, EPC_0 must be measured under conditions that mimic the in situ conditions of the hyporheic zone. Such conditions include ionic strength, pH and the use of fresh samples (Klotz 1991; House et al. 1995; Lucci et al. 2010). Our work suggests that this list should probably include redox status.

4 Conclusions

Our results indicated that the most likely factor to influence or moderate the storage and release of P into baseflow of the Kopuhurihuri Stream was the source of sediment eroded into the stream (e.g. via runoff) and its underlying lithology. The availability of P in subsurface sediments was enhanced at some sites by reducing conditions, but oxic conditions at the surface (0–2 cm) most likely resorbed P onto Fe and Mn oxides from any hyporheic or groundwater P that was upwelling. The measurement of EPC_0 was able to reflect trends in surface water P concentrations at baseflow, but not in hyporheic water at depth. This suggests that to predict their potential influence on baseflow or hyporheic P concentrations, EPC_0 should be measured under the same redox conditions. Furthermore, as baseflow P concentrations strongly reflected the source and chemistry of sediment, efforts to decrease baseflow P concentrations should focus on reducing the erosion of P-rich sediment.

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