



Evidence for the leaching of dissolved organic phosphorus to depth

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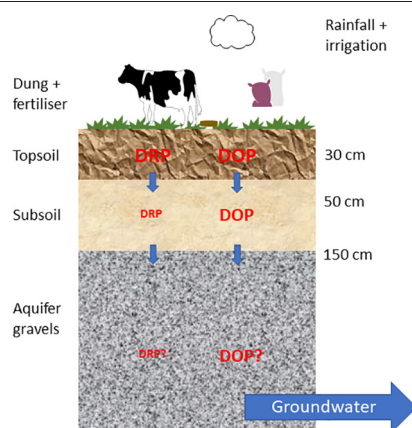
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HIGHLIGHTS

- Very few data are available on the leaching of dissolved organic phosphorus (DOP) from soil.
- Losses of DOP increased relative to dissolved reactive P (DRP) with depth.
- The load of P leached past 50 and 150 cm were similar.
- Most DOP species were leached at a faster rate than orthophosphate through aquifer gravels.
- DOP should be included as part of groundwater monitoring programmes.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphorus (P) can leach from topsoil in inorganic and organic forms. While some evidence has shown inorganic P (orthophosphate) can leach to depth in some soils, less is known of dissolved organic P (DOP). This is not helped by a paucity of DOP data for groundwater. We hypothesized that DOP species would leach in greater amounts to depth and at a faster rate through aquifer gravels than orthophosphate. We applied superphosphate with or without dung to a low P-sorption soil under pasture and irrigation. Between 0.7 (control) and 2.4 (dung + superphosphate) kg P ha⁻¹ was leached through 30 cm with a mean ratio of DRP to DOP of 1.5. At 50 cm, 0.7 and 1.3 kg P ha⁻¹ was leached with the DRP to DOP ratio decreasing to 1.1 due to greater DOP leaching (or DRP sorption). There was little difference in DRP losses measured at 50 and 150 cm depth. All DOP compounds except the monoester – inositol hexakisphosphate were leached at a faster rate than orthophosphate through aquifer gravels. These data suggest that where low P-sorption soils overlay similarly low P-sorption aquifers, DOP may reach groundwater at a faster rate than orthophosphate. Furthermore, as many DOP species are bioavailable to periphyton, our data suggest that DOP should be included in the assessment of the risk of P contamination of groundwater where connection to baseflow could be a long-term stimulant of periphyton growth.

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1. Introduction

Phosphorus (P) is essential for the growth of aquatic weeds and algae. Along with nutrients like nitrogen (N), the enrichment of surface waters can lead to excessive growth of aquatic weeds and algae that can

result in eutrophication. The eutrophication processes can result in fish kills, high treatment costs to make water potable, and reduced recreational values. Studies in the USA and UK estimated \$2.2B and \$160 M USD, respectively are spent annually on cleaning up the direct effects of eutrophication (Dodds et al., 2009; Pretty et al., 2003). As a result, substantial effort is undertaken to prevent losses occurring from land where actions may be more cost effective than in streams (Macintosh et al., 2018).

In assessing the impact of P losses, most attention is given to orthophosphate, which many bioassays have determined is readily bioavailable to aquatic weeds and algae. Dissolved reactive P is approximated to orthophosphate that passes through a 0.45-micron filter and is measured via molybdate-based colorimetry. However, of the P that passes through a 0.45-micron a considerable proportion is unreactive and must be digested before being measured via molybdate-based colorimetry. This is commonly called dissolved organic P (DOP). ³¹P nuclear magnetic resonance spectroscopy and chromatography techniques have been used to isolate many organic P species, they are commonly classified into: monoesters, diesters, phosphonates, and polyphosphates (Cade-Menun and Liu, 2014; Espinosa et al., 1999). Using bioassays some research has also found that many organic P species can be as bioavailable as orthophosphate (Li and Brett, 2013). For instance, Thompson and Cotner (2018) analysed 27 waters from lakes in the Upper Midwest United States and found that the total bioavailability of DOP ranged from 0 to 100% with a median value of 78%.

The enrichment of P in soils is well known to enhance the loss of soil P from land to water in dissolved form via surface runoff and subsurface (viz. leaching) pathways (Haygarth et al., 2000). While many consider surface runoff to be the main pathway of P losses, leaching losses can be significant (McDowell et al., 2019; Stuart and Lapworth, 2016). Factors that exacerbate leaching losses of P include: poor P sorption capacity of the soil, which has been approximated to a lack of aluminium (Al) and iron (Fe) oxides in agricultural soils of pH 4.5–7 (Gu et al., 2019; Liao et al., 2019); a coarse texture or the presence of macropores which enhances drainage (Mabilde et al., 2017); and intensive land use that loads the soil with P either as inorganic fertilisers or organic manures (Azevedo et al., 2018). As inorganic P builds up in soil, so too does organic P, although the rate of inorganic to organic P build up increases with soil P fertility (Boitt et al., 2018).

Research into the movement of DOP is unclear, some have found DOP to be more mobile and in greater concentrations than DRP, while others have found the opposite (Berg and Joern, 2006; Wang et al., 2013). Instances of greater sorption and decreased leaching of DOP through the topsoil have been attributed to the presence of multiple phosphate moieties, such as in inositol hexaphosphates (Giles et al., 2011; Koopmans et al., 2007), while other DOP compounds such as diesters are likely to be poorly sorbed and hence more mobile than DRP (McDowell and Koopmans, 2006; Toor et al., 2003). Some work has also found DOP to be preferentially enriched (96% of total P) in water from artificial drainage networks commonly 0.5–1 m beneath the soil surface (Andersen et al., 2016). If highly mobile, it may be possible for DOP to leach to groundwater. Recently, enriched concentrations of DRP have been noted in response to intensive land use, or high transmissivity coupled with poor soil or aquifer P sorption (Holman et al., 2010; Liao et al., 2019; McDowell et al., 2015; Stuart and Lapworth, 2016). If groundwaters are enriched with P, this could lead to a long-term source of P input into streams at baseflow when the growth of algae is most likely. However, DOP is not commonly measured in groundwater nor has there been any evidence of the leaching of DOP through aquifer gravels.

The aim of this research was to determine the concentrations of DRP and DOP in leachate through topsoil, subsoil, and aquifer material under intensive grazing dairy farming. Additional data was available of leaching to 200 cm where leachate intersected an unconfined aquifer. Our hypothesis was that DOP would be more mobile than DRP and be preferentially leached through topsoil and aquifer materials. We

conducted our study in a region in New Zealand with free-draining and low P-sorbing soils currently seeing an expansion of irrigated, intensive dairying (Carrick et al., 2013a; Golder Associates, 2015). We determined if these soil and land use factors increase the risk the long-term leaching of P to groundwater.

2. Materials and methods

2.1. Catchment description

The sampling sites were located within the 3085 km² Manuherikia River catchment, in the province of Otago, New Zealand. Elevation in the catchment ranges from 150 m above sea level at the outlet to 2300 m in the surrounding Hawkdun, St Bathans and Dunstan ranges. The climate in the catchment is continental with warm summers and cold winters. Mean annual temperature is 10 °C with a range of –20 to 38 °C (Kitto, 2011). Rainfall at the main urban centre, Alexandra is 340 mm, while the mean annual moisture deficit across the catchment is 300 mm (Watkins et al., 2015).

Land use in the catchment is predominantly dryland sheep and beef (76%) or deer (3%) grazing high producing ryegrass or browntop and white clover along the valley floors. Conservation land occupies 11% of the catchment. The remaining land area (25,000 ha) is irrigated pasture grazed by sheep and beef (7%) and a small amount used for dairying and vineyards (3%). Approximately 90% of irrigation water is delivered as flood irrigation while the remainder is spray irrigation (Golder Associates, 2015).

The area of land irrigated is proposed to increase by 20,000–30,000 ha fuelled by an increase in storage and the conversion of inefficient flood irrigation to spray irrigation (Golder Associates, 2015). Considering the cost of supplying water, dairying is one of the few land uses that would be profitable (Watkins et al., 2015). An expansion of dairying on irrigated land will see an increase in the use of P fertiliser, typically from 5 to 10 kg superphosphate ha⁻¹ yr⁻¹ on most dryland properties to 30–45 kg P ha⁻¹ yr⁻¹ on intensive dairy properties (Watkins et al., 2015).

Soils in the catchment are mostly Semi-arid or Recent with smaller pockets of Pallic and Gley soils (New Zealand Soil Classification) (Hewitt, 2010). These soil orders translate to Hapluids, Fluvents, Haplustalfs, and Aquents, respectively in US Soil Taxonomy (Soil Survey Staff, 2014). The Semi-arid and Recent soils are low in carbon (C) and slightly acid to neutral pH with low anion storage capacity (ASC; commonly <10%), a measure used as a proxy for the concentration of Al and Fe oxides and P sorption capacity (McDowell and Kitto, 2013).

Gauging of the Manuherikia River at Ophir shows that flow during summer months is strongly influenced by a dam 35 km upstream and irrigation takes and return flow between the dam and the flow recorder. The seven-day minimum annual low flow set for ecological health is 2.2 m³ sec⁻¹. However, due to drought, flow regularly falls below this. Outside of summer and autumn, flow is typically characterised by rivers fed by snowmelt and winter rain-dominated high flows (Larned et al., 2018).

Most of the available groundwater in the catchment is contained within unconfined, water-table aquifers, which are primarily recharged by irrigation-associated soil drainage. These groundwater systems discharge their excess into the lower Manuherikia. The aquifers are mainly high permeability sandy gravel systems, with a base defined by low permeability silt and mudstone (Otago Regional Council, 2012).

2.2. Site description

The study site was used to extract barrel lysimeters and house two pan lysimeters (Fig. 1). The site was located near Omakau in a paddock of one of the earliest dairy farms to be established in the Manuherikia catchment (2008). The property supported 3.2 cows ha⁻¹ spread over

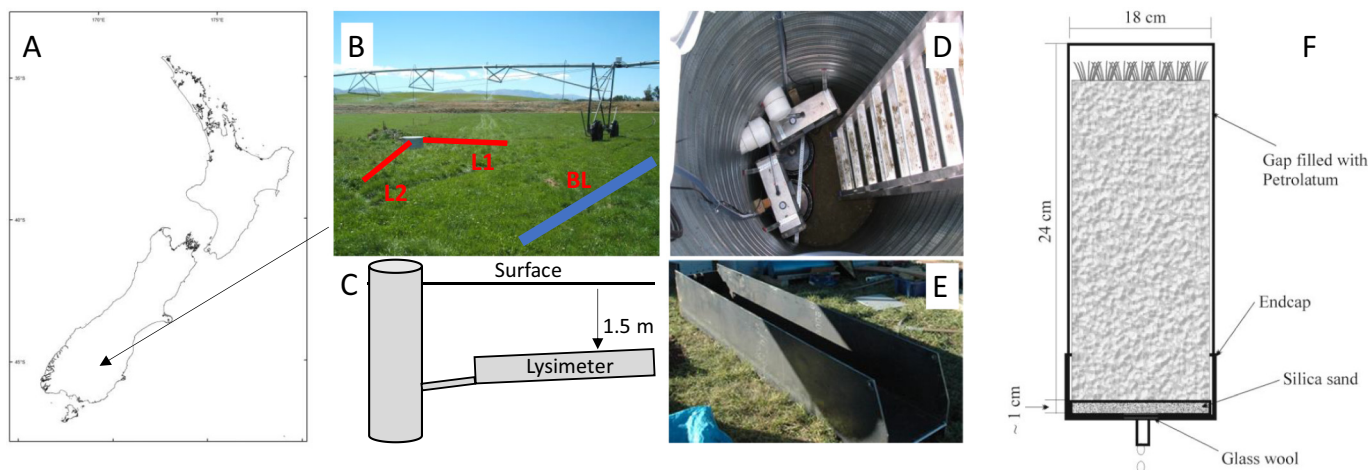


Fig. 1. Details of the experimental pan and barrel lysimeter set-up showing: a) location of the field site in New Zealand; b) location of pan lysimeters under the pivot sprinkler irrigator (L1 and L2); c) location of the pan lysimeters in relation to surface and drainage collection chamber; d) collection chamber with white drainage pipe from each pan lysimeter, tipping bucket drainage monitoring and leachate collection drum underneath; e) 2.2 m long by 0.42 m wide (0.4 m walls) pan inserted 1.5 m depth under the undisturbed soil to channel flow to the collection drum; and f) the construction of a barrel lysimeter taken from location BL on B.

270 ha of flat land ($< 5^\circ$ slope), with an annual rainfall of about 520 mm and evapotranspiration of about 700 mm distributed over September to May. Irrigation is therefore required and applied via a centre pivot system. Irrigation (700 mm) was supplied every four to five days over six months resulting in an average application depth of 5 mm day^{-1} . Nutrients were applied at a rate of 200 kg N ha^{-1} in five applications of 40 kg N ha^{-1} every 30–45 days from October to March, and $45 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ applied in November to January. Pasture was grazed for four days every 25–35 days depending on pasture growth rates.

The soil type across the irrigated footprint is an association of Tarras moderately deep and Eweburn shallow to very shallow loamy silt over gravels, reflecting variation in the depth to gravels across the floodplain, and classified as a Weathered Fluvial Recent soils in the New Zealand Classification, and a Fluvent in US Soil Taxonomy (Hewitt, 2010). In the study site paddock Eweburn soils were predominant, with $> 35\%$ gravels typically occurring within 50 cm of the surface, with rapid permeability ($> 72 \text{ mm hr}^{-1}$) and a low ASC ($\sim 12\%$) in the A-horizon (Landcare Research, 2014). The soil overlays a permeable aquifer of Quaternary alluvium at 2 to 8 m depth with good hydraulic connectivity to the nearby Manuherikia River (Otago Regional Council, 2012). The depth to groundwater is typically 1.5–3.5 m below the soil surface.

2.3. Soil sampling

Soil was sampled in September 2015 at 10 locations along a 20 m transect at the site to 0–7.5, 7.5–15, 15–30, 30–40, 40–50, 50–150, and the 150–250 cm depths. Soils were analysed for ASC (Saunders, 1965), Olsen P (Olsen et al., 1954), organic C via LECO C/N analyser, the percentage stones ($< 2 \text{ mm}$), total P after digestion of soil with aqua regia (Crosland et al., 1995), water extractable P (as an indicator of potential P loss (McDowell and Condon, 2004)) and pH (Hendershot et al., 1993).

2.4. Barrel lysimeters

In late September 2015 the site was used to extract 48 undisturbed monolith lysimeters, each 20 cm internal diameter. Twenty-four lysimeters were taken to 30 cm depth and 24 down to 50 cm depth. These were taken to a lysimeter facility at the Invermay Agricultural Centre in Mosgiel, New Zealand (c 100 km from the site). The facility had a transparent and colourless roof to control rainfall but was open at the sides to allow airflow and maintain conditions as close to the field site as possible. Each lysimeter was taken by carefully excavating around the soil and gently lowering a PVC pipe. A cutting ring was housed within the lower end of the pipe to give a small gap between the intact

soil core and the lysimeter casing. When the pipe had been completely lowered, soil beneath it was cut with a knife to give a 'clean break' at the base. The base of each lysimeter was packed with acid-washed (0.1 M HCl) and neutralised (0.1 M NaOH) silica sand (nominal grain size $< 70 \mu\text{m}$) before a base cap was glued in place. The gap between the soil core and the PVC pipe was filled with petrolatum to seal the intact cores and prevent edge-flow as per Cameron et al. (1992). In the base cap of each lysimeter an outlet hole was made to which suction could be applied and any ponded leachate removed after precipitation events.

Beginning in mid-October 2015, 50 mm of rainfall (reverse osmosis water, with P concentration of less than the detection limit of 0.005 mg L^{-1}) was sprinkled onto each lysimeter over two days, every two weeks for seven months to simulate a typical irrigation season of 700 mm. Leachate was collected after each event. Natural drainage was augmented by applying 50 cm suction during each event, sufficient to drain large pores active in water flow and avoid ponding and anaerobic conditions affecting soil and leachate chemistry near the base of the lysimeter (Carrick et al., 2013b; Weihermüller et al., 2007). Suction was maintained by a vacuum pump and network linked to collection vessels. Herbage was cut regularly, oven-dried and bulked for each lysimeter across the irrigation season.

Treatments were applied at the beginning of November following the first leachate event in October. Treatments consisted of six replicates of each depth receiving either no P (control), dung or superphosphate applied at 45 kg P ha^{-1} or superphosphate + dung applied at 90 kg P ha^{-1} . The dung was sourced from the site by scooping-up fresh dung pats soon after grazing in October, bulking the dung pats together, stirring the bulked sample and sub-sampling for total P. Based on the dry weight total P concentration, a fresh dung pat of 2 kg was applied to the dung treatment and after superphosphate had been applied to the superphosphate + dung treatment.

Leachate was filtered ($< 0.45 \mu\text{m}$) in the field before being analysed colorimetrically (Watanabe and Olsen, 1965) for DRP (also called filterable or soluble reactive P), and total dissolved P (TDP) and total P (TP) after acid persulfate digestion (Eisenreich et al., 1975). Dissolved organic P and particulate P (PP) were calculated as the difference between TDP and DRP and TP and TDP, respectively. Measurements were made of the mass of bulked pasture dry matter and its TP concentration via aqua regia digestion (Crosland et al., 1995).

2.5. Pan lysimeter

As part of another study to determine the susceptibility of this soil and site to leach N, two pan lysimeters were installed at the site (Webb, 2010)

using the method of Carrick et al. (2011) in July 2011. Briefly, the lysimeters consisted of sub-horizontal collector arms that extended outwards from a central vertical 1 m diameter and 2.7 m deep access chamber. The lysimeter arms were 2.2 m long and 0.42 m wide, providing a total measurement area of 0.924 m² per lysimeter. Lysimeter side walls were 0.45 m high, to minimise the risk of divergent sub-surface flow above the lysimeter base (Mertens et al., 2005; Peters and Durner, 2009). Each lysimeter arm was installed at a depth 1.5 m below the soil surface at a 1:30 upward slope. The lysimeter collector arms were installed from within the access chamber using a hydraulic ram which ensures that the overlying soil profile was not disturbed during their installation. Leachate was routed from the lysimeter arms into a central access chamber and collected on an event basis. Leachate samples were collected by the Otago Regional Council until they decommissioned the pan lysimeter in January 2015. The volume of leachate was recorded using a tipping bucket rain gauge, and DRP and TP concentrations determined by a commercial laboratory using the same procedures used in the barrel lysimeters. Unfortunately, DOP was not measured.

2.6. ³¹P nuclear magnetic resonance (³¹P NMR) spectroscopy of barrel lysimeter leachate

To gauge the relative distribution DOP forms leached from the barrel lysimeters and that could be leached through aquifer gravels, a 50 mL subsample of all leachate events from the dung treatment lysimeters was bulked together. The bulked sample (c. 5 L) was filtered (<0.45 µm), frozen and freeze-dried. The resulting freeze-dried sample (2.2 g) was shaken in 40 mL of 0.1 M NaOH + 0.05 M Na-EDTA for 2 h, and filtered (< 0.7 µm, Whatman GF/F glass fibre filter paper). A subsample of 0.1 mL was taken and diluted to 10 mL, this was then analysed for reactive P and TP. The remaining 39.9 mL was frozen and again freeze-dried. The NaOH freeze-dried sample was reconstituted in 2 mL D₂O, ultrasonicated (Crest model 175 T) for 3 min, equilibrated for 20 min and then centrifuged (Qualitron 6 place mini-centrifuge) for 5 min. The supernatant was transferred to a 10 mm NMR tube and ³¹P NMR spectra were obtained using a 10 mm Varian z-axis PFG direct detection probe at 202.298 MHz at 20 °C with a Varian 500 MHz Inova NMR spectrometer with a 51 mm standard Oxford superconducting magnet, FTS temperature controller, dual full-band channels, one low band decoupler channel and a 28-shim set. Accumulation of data was halted after accumulating 18,000 scans (over 16 h) using a pulse angle of 45°, a pulse delay of 7 s to allow for full spin-lattice relaxation times (McDowell et al., 2006), and an acquisition time of 1.99 s with 64 K data points.

Spectra were processed using a Lorentzian line shape of 5 Hz and measured using Mestre-C software (Cobas et al., 2010). Chemical shifts were recorded relative to an external phosphoric acid standard (δ = 0 ppm). Peaks were assigned to P classes using the assignments of McDowell and Stewart (2005). Peaks were made quantitative by combining the percentage spectral area occupied by a class of compound, and the total P concentration in the corresponding extract.

2.7. Aquifer gravel columns

To determine the relative susceptibility of different organic P compounds to leach through aquifer gravels, breakthrough curves were determined using gravels from the site. Gravels were extracted at the same time as collecting the barrel lysimeters by excavating down and extracting 200 kg of soil (hereafter called gravel) from the 1.5–2.5 m depth. Gravels were air dried and sieved to 8 mm to allow gravels to be packed into cylindrical columns of 7.5 cm diameter and 30 cm length (total volume = 1325 cm³). Prior to packing the column, a 3 mm hole was drilled into a base plate and the base plate attached to the column. A nylon mesh with 1 mm sized holes was put over the base plate before

1 kg of air-dry gravel was placed into the column. A plastic connector fitted to the base plate funnelled drainage into a 2 L container. A total of 20 columns were made.

Columns were saturated for 24 h in reverse osmosis water to fill the pore space and allowed to equilibrate and drain for 1 h prior to treatments being applied. The treatments were:

- Unreactive bromide (KBr);
- Orthophosphate (KH₂PO₄; molecular weight, MW = 136.09 g mol⁻¹);
- Four orthophosphate monoesters, *myo*-inositol hexakisphosphate (phytic acid, C₆H₁₈O₂₄P₆.xNa⁺.yH₂O; MW = 660.04 g mol⁻¹), adenosine triphosphate (C₁₀H₁₆N₅O₁₃P₃; MW = 507.18 g mol⁻¹), α-D-glucose 1' phosphate (C₆H₁₁O₉PNa₂.xH₂O; MW = 304.10 g mol⁻¹), D-glucose 6' phosphate (C₆H₁₁O₉PNa₂.xH₂O; MW = 336.32 g mol⁻¹), and guanosine 5' monophosphate (C₁₀H₁₂N₅Na₂O₈P; MW = 407.18 g mol⁻¹);
- Two orthophosphate diesters, 3-sn-Phosphatidyl-L-serine (from bovine brain, C₄₂H₈₂NNaO₁₀P; two variable hydrophobic fatty acyl chains; MW = 815.1 g mol⁻¹), 1,2-Diacyl-sn-glycero-3-phosphocholine (Lecithin comprising of palmitic, oleic, linoleic and stearic acid with an average MW = 768 g mol⁻¹); and
- Two aromatic esters, *para*-nitrophenyl phosphate (C₆H₆NO₆P; MW = 217.09 g mol⁻¹) and Bis 4-nitrophenyl phosphate (C₁₂H₈N₂O₈P; MW = 339.17 g mol⁻¹).

Solutions (1 L) containing each of the compounds dissolved to a concentration of 1 mg P L⁻¹ or 1 mg Br L⁻¹ were prepared the day before application to the columns. All compounds were sourced from Sigma Aldrich Ltd. Treatment solutions were applied by syringe evenly across the tops of the columns at a rate of 33 mL every 10 min for 360 mins. Leachate was collected every 20 mins, filtered and analysed the same day for DRP and TDP via colorimetry, or for Br via an ion selective electrode.

2.8. Statistical analyses

The statistical model used a design with four P treatments and two depths as a factorial, randomised block design with six replicates for lysimeters. Soil samples used the same design but had 10 replicates. All statistical analyses were performed with Genstat Committee (2015). Phosphorus fractions in leachate were subjected to analysis of variance for each event and for the total load from each lysimeter. The corresponding P values for the comparison of treatments means are given along with the least significant difference at the P < 0.05 level of significance.

3. Results

3.1. Soil sampling

Concentrations of WEP, Olsen P, total P and organic C at the site were greatest in the topsoil and declined with depth (Table 1). The ASC also decreased with depth. In contrast, the concentration of stones and soil pH increased with depth. Stones with a sand-textured matrix were especially prevalent beyond 50 cm. The concentration of Olsen P and total P, and the percentage ASC in the deepest samples were <15% of those in the topsoil (0–7.5 cm depth), while WEP concentration was around 20% of that in topsoil. However, with taking the greater stone concentration into account the volume of soil subject to leaching may be greater than in topsoil.

3.2. Lysimeters

Concentrations and loads of P fractions in leachate from the barrel lysimeters are given in Fig. 2 and Table 2, respectively. No differences

Table 1

Mean Olsen P, water extractable P (WEP), anion storage capacity (ASC), organic C and pH for different soil depths at the site.

Depth (cm)	Olsen P (mg kg ⁻¹)	Total P (mg kg ⁻¹)	WEP (mg L ⁻¹)	ASC (%)	Organic C (g kg ⁻¹)	pH	Stones (g kg ⁻¹)
0–7.5	26	818	0.065	14	26	6.1	13
7.5–15	14	663	0.049	7	19	6.3	37
15–30	11	536	0.046	6	10	6.4	110
30–40	9	428	0.039	5	4	6.7	167
40–50	9	418	0.036	3	4	6.7	340
50–150	3	143	0.021	2	2	6.6	680
150–250	2	105	0.014	1	3	6.9	743
LSD ₀₅	10**	165***	0.006***	1***	6***	0.7 ^{ns}	35***

were noted in mean concentrations of P fractions in the event prior to the application of treatments. Following treatment application in early November, DRP, DOP and PP leachate concentrations were enriched for the dung, superphosphate and superphosphate + dung treatments compared to the control treatment. These differences continued for four additional events for DRP at the 30 cm depth and three events in the 50 cm depth lysimeters. Differences in DOP and PP were noted for six and four events, respectively, from both depths.

Losses soon after the application of treatments translated to significant differences between loads over the 13 leaching events (Table 2) Differences were largely driven by the presence of dung, although PP in the superphosphate-only treatment was also enriched compared to the control. The mean total drainage of 200 mm (standard error ± 10 mm) was not different across treatments. Loads of DRP were greater

Table 2

Loads (kg P ha⁻¹) of dissolved reactive P (DRP), dissolved organic P (DOP), particulate P (PP) and total P (TP) leached from each treatment. The least significant difference is given at the P < 0.05 level for the contrast of mean P fraction loads by treatments, depth and their interaction. The corresponding P value for the analysis of variance is also given by the number of asterisks (** and *** equate to P < 0.01 and 0.001, respectively).

Treatment	DRP	DOP	PP	TP
30 cm depth				
Control	0.23	0.22	0.29	0.74
Dung	0.44	0.46	0.89	1.59
Superphosphate	0.53	0.17	0.59	1.19
Superphosphate + dung	0.77	0.73	0.93	2.43
50 cm depth				
Control	0.20	0.20	0.31	0.71
Dung	0.32	0.32	0.60	1.24
Superphosphate	0.27	0.18	0.41	0.86
Superphosphate + dung	0.40	0.30	0.56	1.26
LSD ₀₅ treatment	0.10***	0.06***	0.11***	0.29***
LSD ₀₅ depth	0.07***	0.04**	0.07***	0.21***
LSD ₀₅ treatment × depth	0.14**	0.09**	0.15**	0.42**

than for DOP at the 30 cm depth, but similar at the 50 cm depth due to a reduction in DRP losses. The load of PP also decreased with depth but was still greater than either DRP or DOP.

The quantity of P lost in leachate at 30 and 50 cm was, when added to the amount of P harvested in dry matter, between 16 and 50% of the P applied as either dung or superphosphate (Table 3). For the control treatment, the greatest amount of P removed was

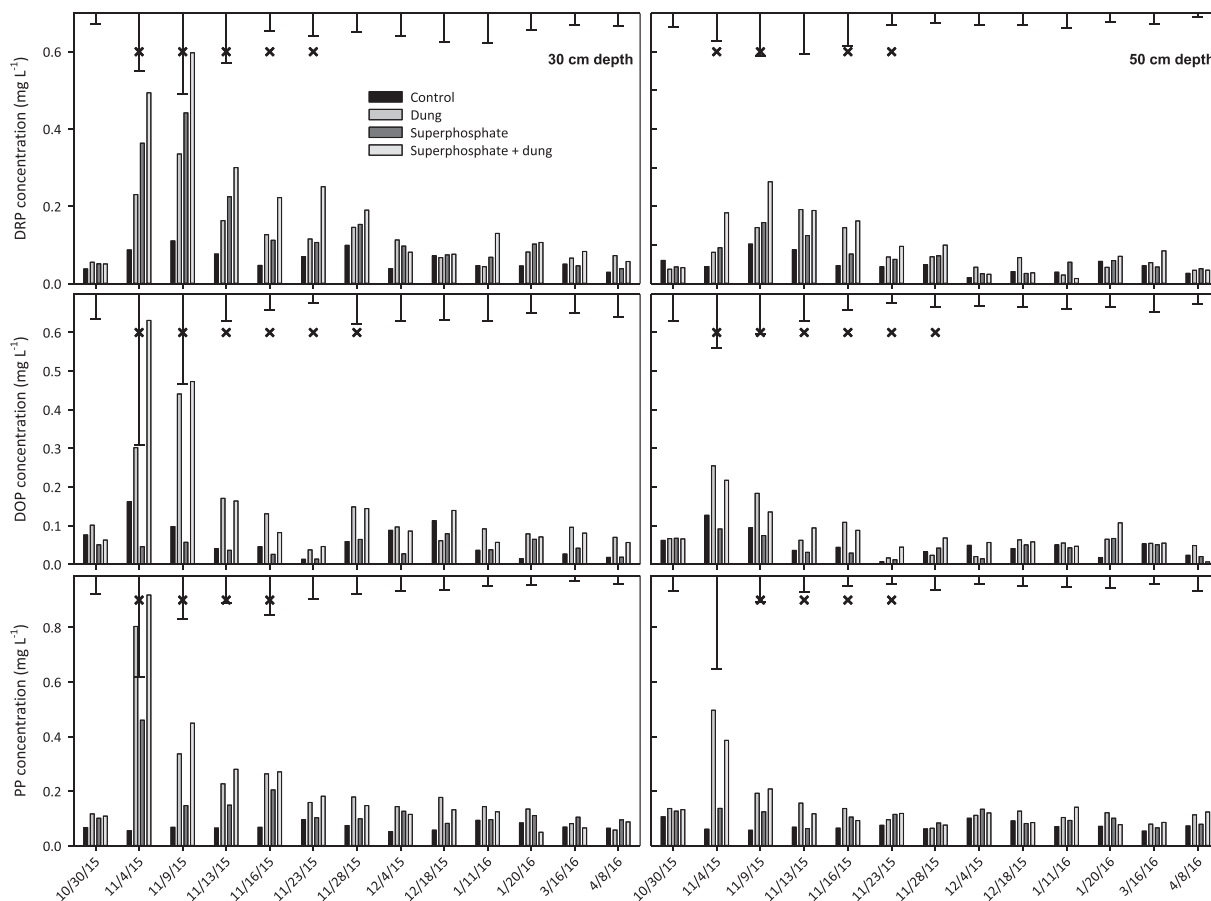


Fig. 2. Mean dissolved reactive P (DRP), dissolved organic P (DOP) and particulate P (PP) concentrations for each treatment and depth by event. The error bars represent the least significant difference at the P < 0.05 level while the cross indicates a significant difference amongst treatments for the event.

7.2 kg P ha⁻¹ (0.7 kg in leachate at 30 cm + 6.5 kg in dry matter) meaning that P removed in herbage or lost in leachate was sourced from P stored in the soil and previous applications of fertiliser.

Additional data were sourced from the Otago Regional Council for two pan lysimeters that sampled leachate at 1.5 m depth from the site sampled for the barrel lysimeters. Losses of DRP and TP in leachate over two irrigation periods in 2012/13 and 2013/14 were 1 and 1.6 kg ha⁻¹, respectively for DRP and 1.6 and 2.1 kg ha⁻¹, respectively for TP (Fig. 3). Losses were enhanced after the application of superphosphate, but quickly resorted to near constant levels. This is consistent with studies of fertilised pasture where there is a sudden flush of available P, followed by an exponential decrease in leaching or runoff losses with time (Burkitt et al., 2011). These losses were within the range reported for the barrel lysimeters suggesting little sorption of P beyond 50 cm depth. However, it is worth noting that despite simulating field conditions as much as possible, rainfall in the barrel lysimeters did not match the intervals seen in the field.

3.3. Leaching of DOP compounds

The results of the ³¹P NMR analysis of leachate from the 50 cm depth indicated that of the TDP detected, 14% was orthophosphate, 44% was as orthophosphate monoesters and the remaining 42% was assigned to orthophosphate diesters (Fig. 4). The signal to noise ratio was too low, and hence too poorly resolved, to assign specific monoesters or diesters. Nevertheless, these data were taken as a strong indication of the presence and potentially high mobility of some DOP species.

The addition of known DOP solutions to the columns of aquifer gravels resulted in breakthrough times (i.e. the time to reach 95% of the maximum leachate concentration) that varied from 100 to 320 min (Table 4, Fig. 5). The two diesters compounds were stopped after 180 min for two reasons. The first was that due to their expense, very little of the solution could be made. The second was that they plateaued early (c. 100–120 min). For context, bromide breakthrough was achieved after 80 min. The total quantity of P sorbed compared to that added was calculated to be between 51% for the aromatic ester – *para*-nitrophenyl phosphate to 74% for the monoester *myo*-inositol hexakisphosphate.

In addition to TP losses, all DOP compounds resulted in DRP being leached (Fig. 5). This varied from approximately 0.6 mg L⁻¹ for three monoesters and one diester to 0.15 mg L⁻¹ for one aromatic ester. The leaching of DRP indicates that orthophosphate had been released as the compound drained through the aquifer gravels. We make no

inference about the origin of this DRP except to say that it could be due to either the hydrolysis of added DOP, desorption of DRP from the soil or mineralisation of soil organic P.

4. Discussion

4.1. Soil characteristics

As discussed below, soil chemical factors that enhance the likelihood of P leaching to depth include soil test P, pH and mineralogy. The risk of P leaching increases with soil test P concentrations – usually associated with intensive land use (Pote et al., 1996), soil pH in the 5.5–7.5 range where P solubility is at its greatest (Lindsay, 1979), and in soils with relatively few Al or Fe-oxides or Ca content to retain P by sorption or precipitation (Nair, 2014; Wang et al., 2015). Soil physical factors likely to enhance leaching include coarse texture and high stone content which together promote high permeability and transmissivity (Carrick et al., 2014; Carrick et al., 2013a). Soil management factors likely to influence P leaching include high rates of P fertiliser application (Dougherty et al., 2011) as also shown with long-term trials, frequent grazing leaving behind P-rich excreta (McDowell et al., 2007) and potentially humic substances that impair P sorption (von Wandruszka, 2006), cultivation (Dodd and Sharpley, 2015; Nash et al., 2015), which can increase the mineralisation and release of P from recalcitrant sources, and irrigation beyond the soil moisture deficit which promotes drainage (McDowell et al., 2019). There is some evidence to suggest that soil with low or extremely high C concentrations may also leach more P than soils with moderate C concentrations (Kjaergaard et al., 2012; von Wandruszka, 2006); however, this is unclear and may be confounded or caused by the presence of one or more of the other risk factors like low concentrations of P-sorbing Al- and Fe-oxides. The site and soil studied exhibited all the risk factors identified above.

4.2. Lysimeter P losses

Treatments explored the range of inputs that are likely to induce P losses, from no inputs (control) to losses from soils with superphosphate and dung applied. Given the number of risk factors identified above it is not surprising that concentrations and loads were enriched relative to other studies of intensively grazed pasture. For instance, McDowell and Wilcock (2008) found 22 plot- to catchment-scale studies with P losses for dairy farms in New Zealand measured from 0.1 to 5 kg P ha⁻¹ yr⁻¹ with an average of 1.0 kg P ha⁻¹ yr⁻¹ (excluding two uncertain measurements of 10 and 10.5 kg P ha⁻¹ yr⁻¹). Losses for dairy farms with 4–6 months grazing in 13 sites in the US and UK ranged from <0.1 to 2.2 kg P ha⁻¹ yr⁻¹ with an average loss of 1.1 kg P ha⁻¹ yr⁻¹ (Kleinman and Soder, 2008). The highest load measured in our study was 2.4 kg P ha⁻¹ in the superphosphate + dung treatment. With dung patches likely to be deposited on about 2% of the paddock (Haynes and Williams, 1993), the effect of this treatment is likely to be minimal. Losses from the dung or superphosphate were lower (1.2–1.6 kg ha⁻¹), but it is important to realise that this was only for half of the year, albeit when grazing was at its most intensive, and losses would likely be somewhat greater.

Interestingly, the load from the dung treatment was greater than from the superphosphate treatment at 30 cm depth. Dissolved organic P or PP found in dung or manure is known to have a weaker affinity for soil P sorption sites than orthophosphate the main form of P in superphosphate (Pizzeghello et al., 2016). Therefore, when applied at the same total P rate, DOP in dung, which may be poorly sorbed to the soil will be preferentially lost in leachate. The high moisture content and presence of other humic compounds in dung are also known to promote leaching over other animal manures (Stutter, 2015; Vanden Nest et al., 2016; von Wandruszka, 2006). Owing to the soil's coarse texture it is also likely that superphosphate applied P was easily washed into the soil but maintained good contact, and therefore opportunity for

Table 3

Total P concentration in dry matter (g kg⁻¹) and the load (kg ha⁻¹) of P removed in herbage for each treatment and depth. The least significant difference is given at the $P < 0.05$ level for the contrast of mean by treatments, depth and their interaction. The corresponding P value for the analysis of variance is also given; *** equates to significance at the $P < 0.001$ level.

Treatment	Dry matter total P (g kg ⁻¹)	P removed in dry matter (kg ha ⁻¹)
30 cm depth		
Control	2.8	6.5
Dung	3.3	19.7
Superphosphate	3.0	7.4
Superphosphate + dung	3.2	20.3
50 cm depth		
Control	2.9	6.1
Dung	3.2	20.1
Superphosphate	3.0	6.5
Superphosphate + dung	3.2	17.9
LSD ₀₅ treatment	0.3	1.0***
LSD ₀₅ depth	0.4	0.7 ^{ns}
LSD ₀₅ treatment × depth	0.4	1.4 ^{ns}

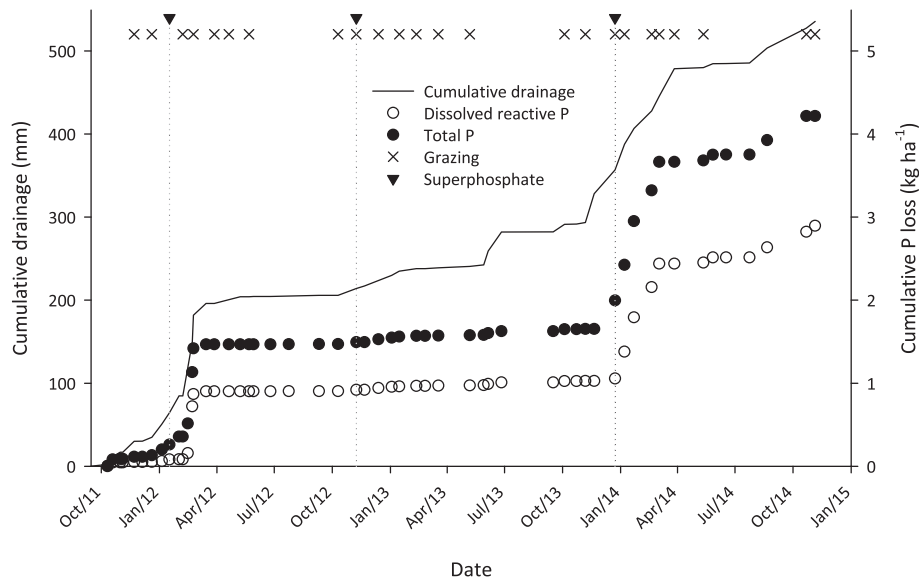


Fig. 3. Cumulative dissolved reactive P and total P in leachate at 1.5 m depth from two pan lysimeters in response to drainage, grazing and applications of superphosphate (45 kg P ha^{-1}) at the Manuherikia dairy farm. Data were sourced from the Otago Regional Council.

sorption, with the soil during matrix flow (Gray et al., 2016). This should result in leachate that was more influenced by soil chemistry and the form of P applied than in those soils where soil chemistry can be negated because leachate bypasses the soil due to macropore flow (Kleinman et al., 2015).

Perhaps of greater interest than losses at 30 cm was the differences in P loads at 50 cm depth. It is well known that organic and inorganic P concentrations in soil stratify, declining with depth as P is sorbed by topsoil (Brock et al., 2007; Sharpley, 2003; Tiecher et al., 2012). However, in soils with low P sorption capacity, here measured as ASC, leaching can occur through deeper, subsoil layers (Andersson et al., 2013; Andersson et al., 2015). This can also be affected by the form of P applied. Indeed, Azevedo et al. (2018) found that the application of cattle, swine, goat and hen manure increased WEP to depth in a sandy

loam soil in Brazil, whereas the application of inorganic fertiliser did not. Furthermore, Chardon et al. (2007) found considerable P in leachate after applying dung to a sandy soil from the Netherlands. Most of this leached P was DOP (called dissolved unreactive P in the paper). In our soil, DOP loads were greatest in the dung and superphosphate + dung treatment, although there was little difference between these treatments suggesting that the application of superphosphate did little to enhance DOP loss (Table 2).

If it is assumed that the 6 months of P losses from shallow lysimeters were could be doubled (at most) to account for losses over the year, then losses from the superphosphate treatment were like those measured annually at 1.5 m depth in the field study. We chose to compare the superphosphate treatment as the dung or dung + superphosphate treatments would only cover about 2% of the paddock (Haynes and Williams, 1993). The similarity in losses infers that there is little attenuation or sorption of P from 0.5 to 1.5 m depth. Unfortunately, DOP was not measured from the pan lysimeter. However, we hypothesize that the leaching and load of DOP would be like that measured in barrel lysimeters. Indeed, Andersen et al. (2016) found that once DOP had left the topsoil it was detected in tile drainage intercepting flow at about 0.8 m depth in Denmark.

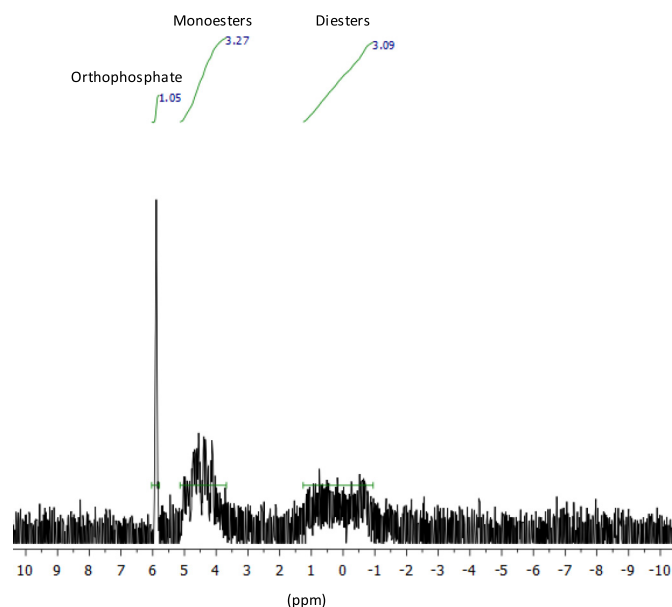


Fig. 4. ^{31}P nuclear magnetic resonance spectra showing the assignment and fit of peaks to P compound classes.

Table 4

Time to 95% of maximum total P concentration in leachate and the total P sorbed during leaching of different dissolved organic P species through the aquifer gravel.

Compound	Time to 95% of maximum total P concentration in leachate (min)	Proportion of P sorbed during leaching
Aromatic ester - Bis 4-nitrophenyl phosphate	180	52
Aromatic ester - <i>para</i> -nitrophenyl phosphate	180	51
Diester - 3-sn-Phosphatidyl-L-serine	100	61
Diester - 1,2-Diacyl-sn-glycero-3-phosphocholine (Lecithin)	120	63
Monoester - adenosine triphosphate	280	64
Monoester - α -D-glucose 1' phosphate	240	56
Monoester - D-glucose 6' phosphate	240	58
Monoester - guanosine 5' monophosphate	280	59
Monoester - <i>myo</i> -inositol hexakisphosphate	320	74
Orthophosphate	320	61

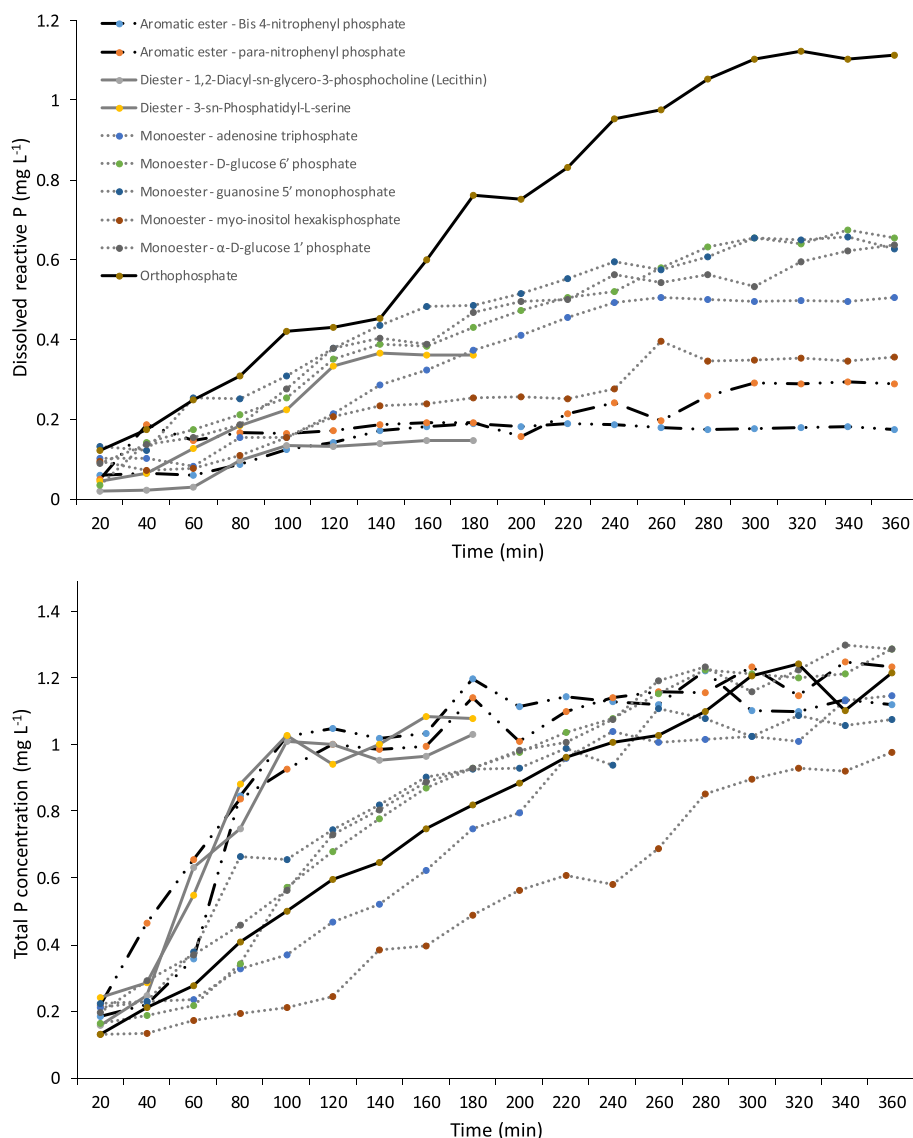


Fig. 5. Dissolved reactive P and total P concentrations of organic P compounds (and orthophosphate) in leachate from the aquifer gravel.

4.3. DOP leaching through aquifer gravels

The reactivity of DOP compounds has been reported to increase with the number of phosphate moieties, but decrease with increasing molecular weight and steric hindrance (Berg and Joern, 2006; Fuentes et al., 2014; Ruttenberg and Sulak, 2011). These findings are based off a few studies comparing a limited range of DOP compounds. For instance, Celi et al. (1999) found that P-rich inositol hexaphosphate was sorbed better to soil than orthophosphate, while Leytem et al. (2002) found the order of sorption to be inositol hexaphosphate > adenosine triphosphate > orthophosphate. Both Wang et al. (2013) and Berg and Joern (2006) found that glucose-6-phosphate was better sorbed than orthophosphate but less sorbed than inositol hexaphosphate. However, like Wang et al. (2013) we found no relationship ($r = -0.46$ $P > 0.05$) between molecular weight and P sorption, measured here as the time to reach maximum concentration in leachate. The absence of a relationship may be caused by the many other factors such as different pH, organic C, pore size and texture, which influence DOP sorption, and the wider range of DOP compounds tested in our study.

It is also important to realise that the leaching of individual DOP compounds may differ to the leaching of DOP compounds when added in combination due to steric hindrance and or the competition of different DOP compounds for P sorption sites. For instance, (Berg and Joern, 2006) found that the sorption of DOP compounds such as adenosine triphosphate or glucose-6-phosphate were lowered when added in combination with orthophosphate than if added individually.

A true indication of the leaching of DOP compounds through aquifer gravels would have measured their concentration in leachate from the lysimeters and aquifer, for example, by ^{31}P NMR. However, although significant progress has been made in the identification and separation of specific DOP compounds in NMR spectra of soil waters and manure, ^{31}P NMR is still too coarse and slow to do this reliably for many samples. For instance, low detection limits (e.g. 100 mg L^{-1}) often require low-P leachate samples to be concentrated by freeze drying, extracted in alkaline (NaOH-EDTA) liquids and detected for 4–24 h. This maximises the extraction of DOP compounds, holds them at a constant pH to facilitate peak identification, and allows sufficient time for P to be detected (Cade-Menun and Liu, 2014). However, the alkaline extraction regime and long detection period often results in the hydrolysis of DOP

compounds meaning that DOP compounds are at best classified into monoesters, diesters, phosphonates etc. (McDowell and Koopmans, 2006). Other techniques such as high-performance liquid chromatography may avoid hydrolysis but are hindered by other compounds (e.g. high organic matter) that interfere in DOP detection (Espinosa et al., 1999).

Our data on the leaching of DOP through the lysimeters, ^{31}P NMR data of leachate, and the leaching of and specific DOP compounds through the aquifer gravels, suggests DOP is preferentially leached through the soil compared to orthophosphate. Furthermore, these data suggest that diesters are both present in leachate and leached at a quicker rate through aquifer gravels than other classes of DOP compounds. In soils, diesters are thought to be more bioavailable to biota than other classes of DOP compounds (Turner, 2008). However, in rivers and lakes, evidence suggests that there is little difference between DOP classes, and that all have similar bioavailability to orthophosphate (Thompson and Cotner, 2018). These findings may be the result of batch studies where long contact periods allow for enzymatic reactions to decompose DOP species into orthophosphate (Giles et al., 2011); however, such conditions are expected in aquatic systems where good mixing occurs.

4.4. Implications for management

The poor sorption and rapid leaching of DOP species through the aquifer gravels infers that there is an enhanced risk of DOP enriching groundwater. However, as DOP is not commonly measured in groundwater a better indication of leaching risk and water quality impact is gained for the behaviour of DRP. High DRP concentrations have been noted in groundwater because of intensive land use alone or in combination with soils of poor soil P sorption capacity. For instance, in the UK, Holman et al. (2010) and more recently Stuart and Lapworth (2016) found evidence of intensive arable land use and sandstone as factors likely to lead to aquifers with enriched groundwater DRP concentrations. In Florida, Liao et al. (2019) found a positive relationship between intensive land use and point sources such as septic tanks, topsoil P concentrations and P concentrations in the vadose and saturated zones of a karst basin. Finally, in a study in New Zealand, McDowell et al. (2015) linked enrichment in groundwater to high soil Olsen P concentrations in soils with low ASC overlying low ASC aquifer gravels. These authors also showed some evidence that DRP concentrations in baseflow of nearby streams mirrored trends in groundwater. Similar links with shallow groundwater and baseflow have been found in studies of alluvial floodplains in Oklahoma (Mittelstet et al., 2011) and sandy soils in Belgium (Mabilde et al., 2017). These data and studies infer that efforts to reduce DRP concentrations in streams by focusing on surface runoff-derived P will be hampered because P is still coming from groundwater under baseflow. Inputs of P under baseflow may also have a greater effect on water quality as stable flows and warmer temperatures allow for periphyton biomass to accrue, whereas during surface runoff, cooler temperatures (at least in temperate climates) and higher flows inhibit growth and flush periphyton away.

The high leachability of the DOP species studied, infers that DOP reach groundwater before DRP, and that leaching will be enhanced in soils and aquifer gravels with low ASC. However, much work remains to identify factors that enhance the risk of DOP leaching. Furthermore, there is a paucity of DOP data, especially from the sampling of groundwater monitoring networks. Without these data, regulatory authorities may be underestimating the risk and potential impact of P on water quality. Much like DRP, the mitigation of DOP from groundwater may take a long time. However, it is uncertain if mitigation will be faster or slower than for DRP as many of the measures designed to prevent P loss focus on DRP or PP fractions, not DOP (Bergström et al., 2015; McDowell and Nash, 2012). For instance, a focus on lowering PP losses by reducing erosion through minimum tillage, resulted in an enrichment of P in topsoil and the loss of highly bioavailable dissolved P into

Lake Erie (Baker et al., 2017; Jarvie et al., 2017). Knowledge of how much and under what conditions DOP leaches or is transformed into DRP is therefore critical to matching an effective array of strategies to mitigate the impact of P on waterbodies.

5. Conclusions

The application of superphosphate with or without dung to a low P-sorption soil under pasture and irrigation led to substantial quantities of P being leached to depth. The proportion of P leached as DOP over DRP was greater at 50 cm than 30 cm depth. There was a suggestion, at least for DRP, that these treatments also caused P to be leached to 150 cm depth. Investigation of the leaching of DOP compounds confirmed that all, but the monoester – inositol hexakisphosphate were leached at a faster rate than orthophosphate. Given that there is little difference in the leaching or bioavailability to periphyton between many DOP compounds or their representative classes compared to orthophosphate this would suggest that DOP should be included in the assessment of the risk of P contamination of groundwater. Where these low P-sorption soils overlay similarly low P-sorption aquifers, there is a high potential for this P to contaminate baseflow where it can be a long-term stimulant of periphyton growth. This knowledge of DOP transfer will therefore enable land managers to better tailor strategies to mitigate the leaching of P and especially DOP.

CRedit authorship contribution statement

RW McDowell: Conceptualisation, Supervision, Formal analysis, Writing-Reviewing and Editing. W Worth: Investigation, Data Curation, Methodology. S Carrick: Data Curation, Writing – Review and Editing.

Declaration of competing interest

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.

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