

Field soil and ditch sediment phosphorus dynamics from two artificially drained fields on poorly drained soils

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ARTICLE INFO

Article history:

Received 14 December 2016

Received in revised form 30 June 2017

Accepted 10 July 2017

Available online 18 July 2017

Keywords:

Phosphorus

Sorption

Drainage water

Attenuation

Soil

Ditch

ABSTRACT

The installation of artificial drains alters soil permeability such that migrating water interacts with soil and sediment biogeochemistry to mobilise or attenuate phosphorus (P). Soil and ditch sediment P chemistry was explored at two artificially drained sites with similar land use, management and drainage class. Site A was characterised by high total P content (282–1437 mg kg⁻¹) and elevated water soluble P (WSP) (10.11 mg kg⁻¹) in a Humic topsoil. Subsurface horizons contained high amounts of leached aluminium (Al) and iron (Fe) and P sorption capacities expressed by the Freundlich K term increased with depth from 338 to 942 mg kg⁻¹. Site B was characterised by low TP (58–476 mg kg⁻¹) and low P sorption capacities (40–173 mg kg⁻¹) that decreased with depth, owing to a high% sand and low Al. Banksides and sediment in the ditch were mostly higher or comparable to P sorption properties measured in subsurface soil horizons from adjacent fields. Dissolved reactive P (DRP) concentrations were monitored in the open ditch, end-of-pipe and in-field piezometers and highest values were recorded in the open ditch (0.03–0.183 mg l⁻¹) at Site A, potentially due to diffuse and point sources on the farm. Higher P concentrations were recorded at end-of-pipe locations compared to piezometers at similar depth, and attributed to a larger contributing area reaching the pipe from the surface and surrounding subsurface layers. Attenuation of WSP by subsoil at Site A was evidenced by low piezometer values (0–0.003 mg l⁻¹). Low P sorption in the ditch at Site B suggests that dredging could expose low P sorbing layers, but adding topsoil could enhance P sorption. Drainage design, maintenance, and measures for P mitigation require an assessment of surface and subsurface P dynamics to ensure a 'right measure right place' approach.

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1. Introduction

Pasture based livestock production systems such as dairy farming rely on grass growth as their primary source of animal feed and can be more complex than other international dairy systems where animals are primarily fed a total mixed ration diet in confinement (O'Mara, 2008). Maximising grass utilisation (growth and trafficability) can be constrained by soils with impeded drainage and low soil fertility. Constraints on agricultural production are often addressed by artificial land drainage to improve soil trafficability, grass growth and extend the grazing season. Artificial drainage networks are designed to direct infiltrating water along lateral subsurface pathways to open ditches or surrounding watercourses. Increasing this connectivity between in-field water and nearby

watercourses carries a risk of nutrient loss that can adversely affect water quality. For phosphorus (P), the process has been conceptualised by Haygarth et al. (2005) as the P transfer continuum where P bound to soil can be mobilised and transported in pathways to a connecting watercourse where it can impact on surrounding water quality. Sources of soil P have been reported to originate from legacy applications that have built up, and recently applied P that is lost via incidental losses during storm events (Wall et al., 2011).

Assigning risk of P loss from fields has identified surface soil test P (i.e. plant available P) and legacy P as the source of P, but where subsurface pathways dominate most risk assessment schemes rarely considers the role of subsoil in P transfer. In managed grassland available P tends to accumulate at the soil surface with concentrations decreasing with depth in sub soil layers (Daly and Casey, 2005). Lower P concentrations in subsoil layers could allow for sorption of P mobilised from the soil surface in vertical pathways and recent studies have alluded to P attenuation at catchment scale where areas of the landscape can attenuate P thus

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creating dis-connectivity along the transfer continuum preventing delivery of P to receiving waterbodies. This has been reported in karst systems in which biogeochemical attenuation of P by calcium (Ca) has attenuated P transfer to groundwater (Mellander et al., 2012; Fenton et al., 2016) and in surface water-fed catchments characterised by high P fixing soils (Mellander et al., 2016; Shore et al., 2016; Daly et al., 2015).

At the sediment water interface, the source/sink dynamics of P reported in rivers and lake systems are complex processes driven by physicochemical properties such as pH, redox, Fe, Al, Ca, organic matter content, particle size distribution, sediment and pore-water P speciation and equilibrium P concentration in overlying water (Reddy et al., 1999). These interactions are poorly understood in drainage systems where the design and engineering hinges on redirecting water towards subsoil layers that can act as either source or sink for nutrients. End-of-pipe remediation systems (e.g. denitrifying bioreactor) or permeable reactive interceptors (Christianson et al., 2015; Fenton et al., 2016; Fenton et al., 2016) rarely consider the interaction of soil and subsoil biogeochemical characteristics with drainage water before installation. As water moves through artificial subsurface drains and open ditch networks it can access soil and subsoil chemical components that can both mobilise and attenuate P. As surface water can transport agricultural nutrients from the soil surface, these nutrients can continue to be mobilised through the network of artificial subsurface drains and open ditches, or, potentially attenuated through the interaction with soil minerals such as aluminium (Al), iron (Fe) and Ca that have a strong affinity for P (Daly et al., 2015; Shore et al., 2016). In grassland mineral soils, these elements are associated with P sorption and retention processes (Paulter and Sims, 2000; Maguire et al., 2001; Daly et al., 2015; McLaren et al., 2014) through the provision of sorption sites on clay surfaces. However, for high organic matter (OM) soils, such as organo-mineral soils, the presence of large amounts of OM occludes sorption sites provided by clay minerals and reduces sorption capacity and P retention (Guppy et al., 2005; Daly et al., 2001). In Irish grasslands Daly et al. (2001) demonstrated that P in these soils remains in soluble form and is prevented from adsorption onto the soil matrix, by the occlusion of sorption sites by OM. Whilst soil Al, Fe and Ca can promote sorption, elevated OM can prevent this process and P remains in the soil solution, available for transfer into connecting waters. As drainage networks are designed to redirect surface water and increase connectivity to open ditches and watercourses, the extent to which this poses a risk of P loss depends on what soil chemical components drainage water encounters along such migration pathways (overland flow, vertical, lateral or groundwater pathways). An important function of soil-water interaction is water purification by nutrient attenuation which varies according to soil characteristics (Schulte et al., 2014). Overall environmental sustainability of sites could include an assessment of the water purification function and a key question on any intensive managed grassland site is to assess if drainage installation and maintenance (open ditches) alters the soil water purification function, thereby leading to water quality issues.

This work examined the P dynamics of surface and subsurface soils (in-field and open ditch locations) and ditch sediments from artificially drained fields with adjacent open ditch networks. The objective was to assess their potential for mobilisation and attenuation of P through interpretation of their P sorption and desorption characteristics. A sub-objective of this study was to examine the interaction of soil biogeochemical properties with drainage water from surface and subsurface monitoring sites at field scale. Using two case-study sites, we describe and compare P characteristics in soil and ditch sediment, alongside water quality results from two fields with artificial drains installed in 2013. This study looks at the soil and sediment biogeochemistry within the first 2 years of installation during the 'settling down' of backfill materials at

the sites. Both fields with receiving ditches were described by soil types with similar drainage class (impeded/poor) but contrasting biogeochemical characteristics.

2. Materials and methods

2.1. Site descriptions and sampling locations

Two commercial farms situated in the south-west of Ireland were used in this study and are currently part of a drainage programme which aims to improve managed grassland productivity and utilisation on poorly-drained soils. This study used fields located on both farms as case study sites, denoted here as A and B, within which, artificial drains were installed in June 2013 on approximately 2 ha of each farm. Drains were installed at 1.1 m depth at site A and 1.7 m depth at site B, surrounded by a gravel pack followed by subsoil and topsoil backfill.

The sites are located, 87 km apart, within regions where impeded or poor soil drainage (O'Sullivan et al., 2015) coupled with climate (precipitation less evapotranspiration) inhibits potential for production and on-farm profitability. Sites A and B are depicted in Figs. 1 and 2, respectively. Annual average (30 year) rainfall in the vicinity is 981.8 mm at Site B and 1621.5 mm in Site A, while annual evapotranspiration is approximately 480 mm in Site B and 430 mm in Site A. A met station was installed at each site, which enabled local rainfall data to be coupled (15 min resolution) with flow data ($\text{m}^3 \text{ day}^{-1}$) measured by calibrated in-stream flumes (Corbett Concrete, Cahir, Tipperary) in tandem with mini-divers (Eijkkelkamp Agrisearch Equipment, Giesbeek, Netherlands) which monitored water flow rate in open ditches upstream and downstream of both drained sites. Flow data at site B was captured for only a portion of this monitoring period from 21/10/2015 to 6/5/2016.

Both sites are located on dairy farms with rotationally grazed permanent pasture and were stocked at rates of 2.38 and 2.47 cows per hectare on the grazing platform, respectively, during the study period. Agronomic soil testing for P was carried out on field composite samples taken to 10 cm depth and extracted using Morgan's reagent (Peech and English, 1944) and values of 1.8 and 6.5 mg l⁻¹ were recorded at site A and B, respectively. Nutrient management plans for both farms were developed based on soil test results and management data to match P inputs with offtakes (Lalor and Coulter, 2008). Site A received 45 kg P ha⁻¹ in 2015 and 52 kg P ha⁻¹ in 2016. Similarly, site B received 48 kg P ha⁻¹ in 2015 and 39 kg P ha⁻¹ in 2016, in line with typical fertiliser application rates on both farms. The timing and rates of P applications during the water quality monitoring period are included in Figs. 6 and 7. For more precise field scale soil classification, farms were soil surveyed at a 1:10,000 scale. At each site, soil profiles were excavated to approximately 1 m and samples from each soil horizon were collected, analysed and archived. Both soil profiles were classified as poorly drained. Poorly drained here is defined as those showing mottling throughout the profile and have an argic (very high clay) or spodic (high in Fe, presence of Fe pan) horizon resulting in stagnation (Schulte et al., 2015).

Bankside and sediment samples were collected along the 100 m reach of ditch at Site A at 2 locations marked on Fig. 1 corresponding to the inlet (A1) and outlet (A2) points in the direction of flow along the ditch. Monthly grab samples of open ditch water were collected the same points (A1 and A2) and water collected from the end-of-pipe from an artificial drain feeding into the ditch at a mid-location along the ditch marked on Fig. 1. In addition, subsurface water was collected from an in-field piezometer (fully screened) at 1 m depth in the middle of the field and marked on Fig. 1. Bankside samples in the ditch were taken at 3 depths (25 cm, 65 cm and 1.1 m – end-of-pipe depth) and sediment samples were collected from the base of

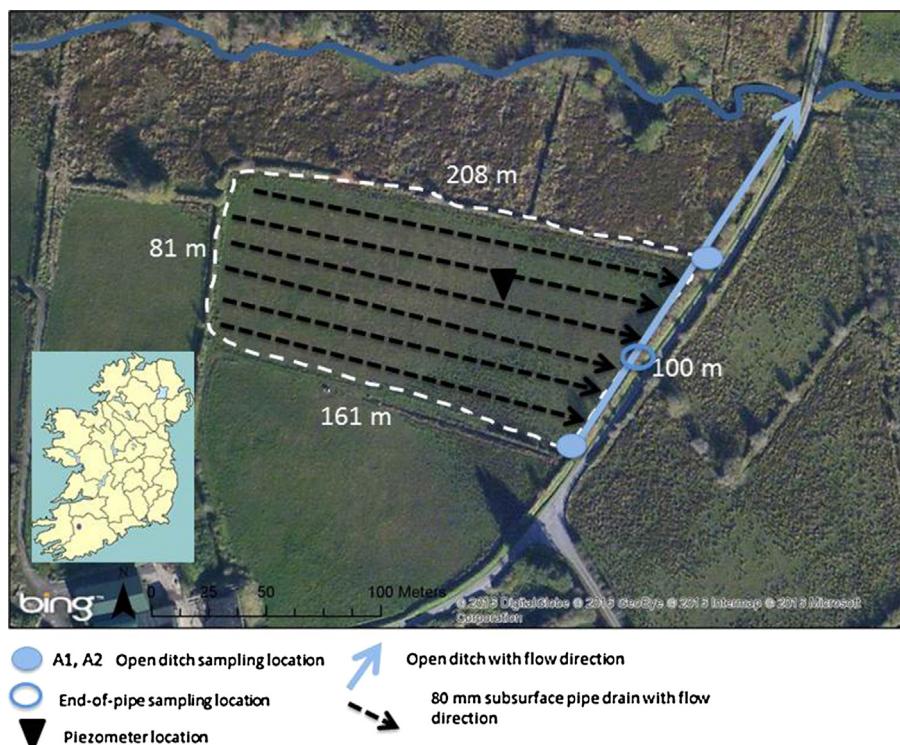


Fig. 1. Site A with locations marked where bankside and sediment samples were taken. Open water ditch and end-of-pipe water samples were collected from the ditch with location of in-field subsurface piezometers.

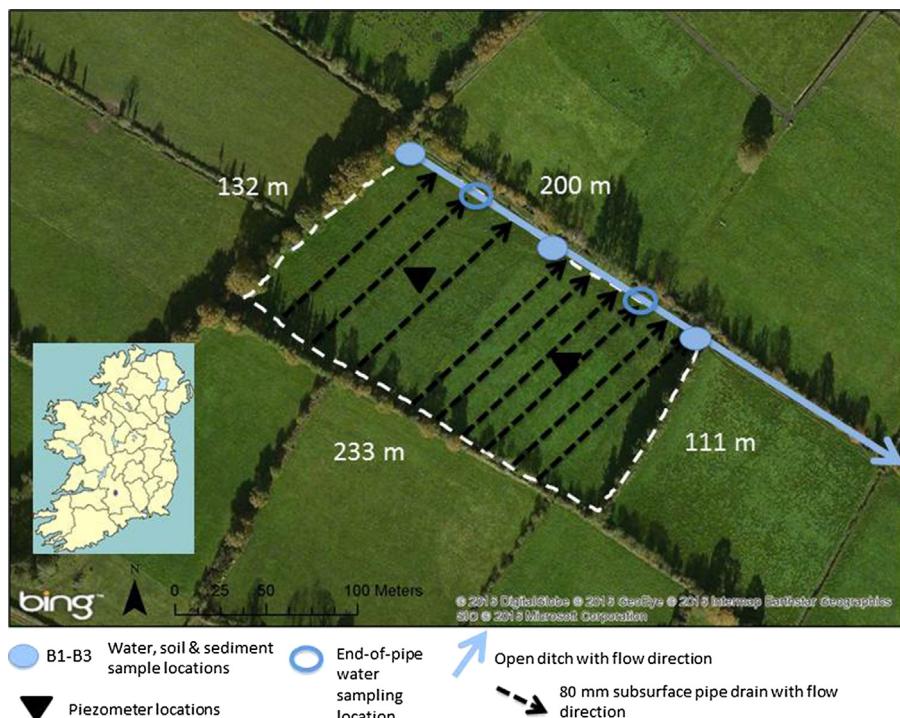


Fig. 2. Site B with locations marked where bankside and sediment samples were taken. Open water ditch, and end-of-pipe water samples were collected from the ditch with location of in-field subsurface piezometers.

the drain at 1.9 m. Locations along the ditch for bankside samples coincided with inlet (A1) and outlet (A2) locations along the ditch at Site A marked on Fig. 1

Along the 200 m reach of open ditch at site B (Fig. 2), bankside samples were taken 1 m and 1.7 m depth, and open ditch sediment

samples were taken at 1.9 m depth. These samples (at three depths) were taken at 3 positions along the open ditch corresponding to the inlet, middle and outlet sections of the ditch and denoted on Fig. 2 as B1, B2 and B3 following the direction of flow in the ditch. Water quality grab samples were taken from the open ditch at the same

Table 1

Soil biogeochemical properties measured from each horizon sampled during soil survey at Site A and B. Biochemical properties are represented by total Al, Fe, Ca and extractable forms using Mehlich3 reagent of the same elements with horizon % organic matter (OM) and pH, physical properties are represented by % sand, silt and clay.

Horizon	Depth to	Clay	Silt	Sand	OM	pH	M3Al	M3Fe	M3Ca	TAl	TFe	TCa
		cm	%			mg/kg						
Site A												
Ap	25	36	49	15	15.6	5.4	825	481	1996	10353	32618	3113
Bs	65	25	54	21	5.9	5.9	1109	441	1991	10382	39675	2305
Cr	110	21	40	39	5.0	5.9	1252	209	693	19347	48972	880
Site B												
Apg	28	15	16	69	4.6	5.9	489	442	1024	5897	13893	1493
Eg	50	4	8	88	0.7	6	191	226	240	1741	6755	350
C	90	14	27	59	1.5	5.9	377	104	659	5469	22486	796
Cr	140	14	17	69	1.1	6.9	272	152	560	3546	16719	890

points (B1–B3) and from 2 artificial drainage pipes (1.7 m depth) at end-of-pipe points feeding into the ditch at locations marked on Fig. 2. Two in-field piezometers (fully screened) at Site B were installed at 1 m depths in the centre of the field at locations marked on Fig. 2. Monthly filtered (dissolved reactive P (DRP), total dissolved phosphorus (TDP)) and unfiltered (total phosphorus (TP), total reactive phosphorus (TRP)) grab samples (50 ml) were taken between June 2015 and May 2016 at each site. Dissolved reactive P was monitored at site A from 3/7/2015 to 31/5/2016, and at site B from 9/7/2015 to the 6/5/2016.

2.2. Soil and water analyses

Soil and sediment samples were dried and sieved to 2 mm and stored in boxes prior to chemical analysis. Soil pH on all soils was determined on a 2:1 soil-water ratio paste and percentage OM estimated from all soils as the loss-on-ignition of 5 g samples (Gavlak et al., 2003). Soil particle size and texture was recorded for each horizon using the hydrometer method (Gavlak et al., 2003). Mehlich3-P (M3P) was determined on all soil using the modified Mehlich test (Mehlich, 1984) to extract P, Al, Fe, Ca at a 1:10 soil solution ratio using Mehlich3 reagent (0.2M CH₃COOH + 0.25M NH₄NO₃ + 0.015M NH₄F + 0.13M HNO₃ + 0.001M EDTA). Total P, Al, Fe and Ca was determined on 1 g soil using microwave digestion (Kingston and Haswell, 1997) followed by ICP-OES analysis. Water soluble P (WSP) was determined on 1 g sample suspended in 40 ml distilled water and equilibrated for 1 h on an end-over-end shaker (Van der Pauw, 1971) before filtration using Whatman No.2 filter paper. Water soluble P in solution was determined colorimetrically (John, 1970).

Dissolved reactive P samples were obtained by filtering duplicate samples (0.45 µm filters, Sarstedt – Filtrpur S 0.45), which were then analysed colorimetrically. Collected water samples were filtered through a 0.45 µm filter and a sub-sample was analysed calorimetrically for DRP, using a nutrient analyser (Aquachem Labmedics Analytics, Thermo Clinical Labsystems, Finland). A second filtered sub-sample was analysed for TDP using acid persulphate. Unfiltered water samples were analysed for TP with an acid persulphate digestion and TRP using the Aquachem Analyser. Particulate P was calculated by subtracting TDP from TP. The DRP was subtracted from the TDP to give the dissolved un-reactive phosphorus (DUP).

2.3. Phosphorus sorption isotherms

Phosphorus sorption isotherms were derived for each soil horizon at both sites and for bankside and sediment samples taken from the inlet (A1) and outlet (A2) points along the open ditch at Site A and at locations inlet (B1), middle (B2) and outlet (B3) locations at Site B. Using a modification of the standardised batch technique by

Nair et al. (1984), subsoil and open ditch sediment samples were equilibrated with P in solution and the data was evaluated using the Langmuir model (Paulter and Sims, 2000). Six solutions of P concentration 0, 5, 10, 15, 20 and 25 mg l⁻¹ were added to 2 g soil samples in 30 ml centrifuge tubes, in duplicate. The suspensions were shaken at room temperature for 24 h, centrifuged and filtered, and the concentration of P in solution was measured colorimetrically (John, 1970). Phosphorus sorbed to the soil was calculated as the difference between initial concentration and P concentration measured at equilibrium. Adsorption data and affinity constants were determined by fitting sorption data to both Langmuir and Freundlich isotherm equations using S (P sorbed) (mg P kg⁻¹) and C, the equilibrium P concentration (mg P l⁻¹). The Langmuir model is expressed as: C/S = 1/Smax*k + C/Smax, where and the Freundlich model as: Log S = Log K + nLog C. The linear forms of both equations were used to derive Smax and K, the sorption maximum (mg P kg⁻¹) parameters; and k and n, the constants related to the binding energy (1 mg⁻¹). A single point sorption index was derived using 1 g soil or sediment shaken with 20 ml solution containing 75 mg P l⁻¹ using the method described by. Samples were shaken on an end-over-end shaker for 18 h and P concentration in solution was measured colorimetrically (John, 1970). A P sorption index (PSI 1 mg⁻¹) was expressed by the equation X/Log C where X is P sorbed (mg kg⁻¹) and C is the final P concentration at equilibrium (mg l⁻¹).

3. Results & discussion

3.1. Soil characteristics at both sites

The soil type at site A was described as Humic Brown Podzolic with high organic matter (OM) in the topsoil. The soil profile is characterised by 4 horizons, with a silt clay loam Ap horizon with high OM content and silt loam Bt and Cr subsoil horizons on top of a bedrock or R horizon. The rich red-brown colour in the Bt horizon and iron on the surface of soil aggregates provided evidence of podzolization occurring at this site. Translocation of topsoil OM to subsurface horizons was evident by the presence of humus coatings on soil aggregates in the Bs horizon. Physical and biogeochemical properties of the surface and subsurface soil horizons at this site are presented in Table 1. Soil samples from the Ap horizon at this site had highest values of OM and lowest pH values compared to subsurface horizons, presenting an acidic organic layer at the surface, typical of organo-mineral soils (Gardiner and Radford, 1980). The subsurface horizons (Bt, C) were predominantly mineral in nature (5.9 and 5% OM) with a neutral pH (5.9). Evidence of the podzolisation process can be seen in extractable and total forms of Al and Fe, which increase down the soil profile. Mehlich3 extractable Al (M3Al) increased from 825 to 1252 mg kg⁻¹ along the profile, indicative of leaching of Al through the soil profile. Similarly, total Al (TAl) and total Fe (TFe) increased from 10,353 to 19,347 and 32,618

Table 2

Soil profile phosphorus data at sites A and B, represented by Langmuir Smax, k and Freundlich K, n with R² values derived from data fitted to both models. Soil P properties are represented by Total P and extractable forms using Mehlich3 reagent and water soluble P (WSP).

Location	Langmuir					Freundlich					WSP	M3P	TP
	Depth to	Smax	k	R ²	PSI	K	n	R ²					
		cm	mg kg ⁻¹	l mg ⁻¹		mg kg ⁻¹	mg kg ⁻¹	l mg ⁻¹					
Site A													
Ap	25	n/a	n/a	0.64	411	338	0.89	0.96	10.11	29	1437		
Bs	65	476	0.35	0.92	424	632	0.82	0.91	0.12	2	282		
Cr	110	435	5.75	0.98	455	942	0.99	0.85	0.13	2	636		
Site B													
Apg	28	333	1.58	0.98	174	173	0.32	0.99	2.16	49	476		
Eg	50	98	0.84	0.99	29	47	0.24	0.99	0.29	14	58		
C	90	145	0.76	0.96	69	46	0.47	0.97	0.16	3	121		
Cr	140	123	0.96	0.99	40	40	0.46	0.96	1.79	6	260		

Table 3

Phosphorus (P) sorption expressed by Langmuir and Freundlich isotherm models; Mehlich3 extractable P, Al and Fe; Water soluble P (WSP), total P (TP) and % organic matter (OM) taken from subsoil bankside and sediment open ditch locations from Sites A and B at locations and depths along the drainage ditch. Pipe here is at the end-of-pipe discharge point, and Base refers to sediment in open the ditch.

Location	Langmuir					Freundlich					WSP	M3P	TP	M3Al	M3Fe	M3Ca
	Depth	OM	Smax	k	R ²	PSI	K	n	R ²							
			m	%	mg kg ⁻¹		mg kg ⁻¹	l mg ⁻¹								
Site A																
A1.0.25	0.25	6.7	588	8.5	0.99	484	2663	1.0	0.92	0.08	7.98	1597	238	385		
A1.0.65	0.65	5.0	526	9.5	0.95	451	5687	1.3	0.81	0.28	2.27	1551	287	71		
A1.Pipe	1.1	4.7	556	18	0.99	383	8441	1.3	0.84	0.00	1.88	1616	169	61		
A1.Base	1.9	4.9	345	5.8	0.97	464	280	0.48	0.91	0.44	16.19	871	531	964		
A2.0.25	0.25	12.2	556	9	0.97	449	1878	0.96	0.86	0.20	9.74	1078	411	600		
A2.0.65	0.65	6.8	476	42	0.94	417	n/a	n/a	0.65	0.00	3.41	1705	272	278		
A2.Pipe	1.1	5.7	370	5.4	0.98	445	n/a	n/a	0.49	0.08	15.26	965	312	755		
A2.Base	1.9	5.3	417	30	0.98	472	n/a	n/a	0.66	0.00	3.57	1291	438	170		
Site B																
B1.1m	1	1.2	159	1.70	0.99	67	53	0.58	0.91	0.22	<5	163	234	104	812	
B1.Pipe	1.7	2.5	385	1.13	0.94	248	179	0.75	0.88	0.23	<5	595	52	163	7756	
B1.Base	1.9	2.9	417	1.33	0.85	290	264	0.81	0.86	0.28	<5	626	93	346	6480	
B2.1m	1	1.4	96	0.51	0.98	67	53	0.58	0.91	0.22	<5	176	234	104	812	
B2.Pipe	1.7	0.8	96	1.44	0.99	248	179	0.75	0.88	0.23	<5	195	52	163	7756	
B2.Base	1.9	2.3	222	0.82	0.99	290	264	0.81	0.86	0.28	<5	212	93	346	6480	
B3.1m	1	2.6	164	0.76	0.81	157	48	0.61	0.98	0.45	<5	79	203	158	1015	
B3.Pipe	1.7	0.6	100	0.70	0.86	102	28	0.50	0.96	0.25	<5	278	116	89	339	
B3.Base	1.9	1.4	196	0.65	0.91	169	81	0.32	0.94	2.75	30.4	163	91	371	1955	

to 48,972 mg kg⁻¹ respectively, as soil depth increased. Phosphorus fractions at the surface horizon were high; 1437 mg kg⁻¹ TP was recorded at the surface and labile inorganic (M3P) and readily desorbable (WSP) (Table 2) fractions were 10 times higher than subsurface values, even-though composites samples to 10 cm recorded low agronomic values based on the Morgan's P test. Particle size analysis at this site indicated a silt clay loam texture with compaction evident in subsurface horizons and accumulation of OM at the surface due to high rainfall and stagnation at the surface, leading to this being classed as poorly drained (Tables 3 and 4).

Soil profile data representative of site B are presented in Table 1. The soil type at this site was classed as a surface water gley, typical of much of the soils across the farm. The soil profile revealed a loamy sand texture at the surface Apg horizon with red-brown colour and sandy loam at the subsurface Eg, C and Cr horizons. The Eg horizon was comprised 88% sand with loose structure in places with low pore space and stagnation likely. There was no evidence of mottling in the C horizon and coarse texture Cr horizon was described underneath. This Apg horizon is characteristic of mineral soils under grassland in Ireland with 4.6% OM at the surface falling to values between 0.7 and 1.5% in subsurface horizons (Gardiner and Radford, 1980). Soil pH ranged from 5.9 to 6.9 along

the profile. Extractable forms of Al, Fe and Ca were highest at the surface horizon compared to subsurface layers. Highest values TP, M3P and WSP were measured at the surface Apg horizon, which is expected, given that agricultural nutrients such as P are applied and managed at the soil surface in grassland based systems. Total P and WSP were lowest in the Eg horizon, potentially due to high sand content (88%) in this layer (Table 2).

3.2. Phosphorus sorption properties at both sites

Phosphorus sorption isotherms derived for each soil horizon at both sites are presented in Fig. 3 to illustrate the contrasting P sorption properties between the sites. The sharpest P sorption curves were produced at Site A indicative of high P sorption properties, compared curves derived for Site B. At Site B the isotherm derived from the first (Apg) horizon produced a steeper curve compared to subsoil horizons at this site. Sorption curves plotted for the subsurface Eg horizon at site B indicated low P sorption capacities compared to Apg horizon. The Langmuir and Freundlich models were fit to these data with varying results. The Langmuir model gave a poor fit ($R^2 = 0.64$) to the data derived from the humic Ap horizon at site A however the same data provided an excellent fit

Table 4

Summary statistics of phosphorus concentrations and speciation in water samples taken from open ditch, end-of-pipe and in-field shallow piezometer at sites A and B.

Location		DRP	TDP	TRP mg P l ⁻¹	TP	PP	DUP
Site A	Ditch	Min	0.003	0.014	0.048	0.000	0.000
		Max	0.183	0.238	0.350	0.166	0.160
		Mean	0.059	0.108	0.074	0.024	0.051
		median	0.055	0.093	0.059	0.008	0.037
End-of –Pipe		Min	0.002	0.004	0.004	0.000	0.000
		Max	0.194	0.563	0.853	0.290	0.369
		Mean	0.047	0.143	0.074	0.043	0.087
		median	0.009	0.030	0.006	0.031	0.016
Piezometer		Min	0.000	0.002	0.000	0.000	0.000
		Max	0.005	0.027	0.009	0.059	0.032
		Mean	0.003	0.008	0.003	0.020	0.011
		Median	0.003	0.005	0.003	0.010	0.007
Site B							
Ditch		Min	0	0.002	0.003	0.001	0
		Max	0.084	0.135	0.067	0.308	0.173
		Mean	0.019	0.036	0.023	0.049	0.014
		Median	0.015	0.03	0.021	0.035	0.003
End-of-Pipe		Min	0	0	0	0	0
		Max	0.011	0.023	0.011	0.026	0.013
		Mean	0.002	0.005	0.003	0.007	0.003
		Median	0.002	0.004	0.003	0.005	0.002
Piezometer		Min	0	0.004	0.003	0.012	0.008
		Max	0.06	0.14	0.112	0.573	0.433
		Mean	0.011	0.039	0.021	0.135	0.096
		Median	0.004	0.021	0.007	0.057	0.038

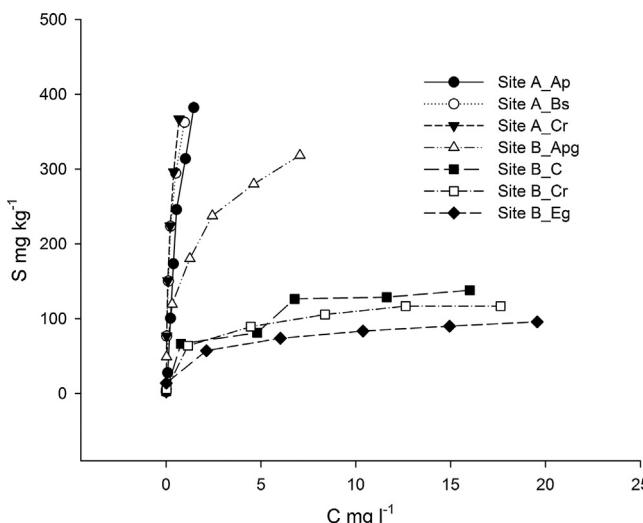


Fig. 3. Isotherms curves of P sorbed (S) plotted against final solution P concentration at equilibrium (C) for soil horizons Ap, Bs and Cr horizons at Site A, and, Apg, E, C and Cr horizons at Site B.

to the Freundlich model ($R^2 = 0.96$). It is possible that the sorption process in this horizon could not be expressed by the Langmuir model or was confounded by high organic matter in the sample. The Langmuir sorption isotherm models have been closely correlated with sorption of P onto Al and Fe surfaces on mineral soils with low OM in Ireland (Daly et al., 2015; Maguire et al., 2001) and elsewhere (Burkitt et al., 2001; Paultre and Sims, 2000; Nair et al., 1998) and it is suggested here that the high% OM may have led to interference by OM on Al-P sorption processes expressed by the Langmuir model. Whilst some studies have reported that the effects of OM on P sorption were unclear (Debicka et al., 2016), others reported that organically bound Al and Fe in high OM soils was less effective for P sorption (Kang et al., 2009; Janardhanan and Daroub, 2010).

Furthermore, Janardhanan and Daroub (2010) reported that P sorption in mineral and OM rich soils was comparable when results were expressed on a mass basis, but when results were reported on a volume basis P sorption was higher for mineral soils. In our study, both Langmuir and Freundlich models provided a good fit to data for most of the samples, with some exceptions, mostly at Site A, namely the Ap horizon of the soil profile and some of the bankside and sediment samples from the ditch at Site A. To allow comparison between sites, isotherm model parameters were not reported where the data did not provide a good fit ($R^2 < 0.7$). Subsurface horizons at site A, with higher Al and lower% OM, provided a good fit to both the Langmuir and Freundlich models ($R^2 > 0.85$). Freundlich K values in the subsoils Bs and C horizons at this site were 2 and 2.8 times higher, respectively, than the value measured in Ap humic horizon. Podzolisation of Al and Fe into subsurface horizons at site A potentially provided more sites for P sorption where highest values were recorded. Isotherm data measured at site B gave an excellent fit to both the Langmuir and Freundlich models although lowest sorption parameters were captured at this site. In the subsurface horizons, potentially due to high% sand low Al and Fe in the subsurface horizons. Single point sorption indices (PSI) reflected isotherm parameters derived from the models. Compared to site A, Site B site presented lowest P sorptive and retention properties expressed as either isotherm parameters or PSI.

3.3. Phosphorus sorption properties in open ditches at both sites

Sorption isotherms derived from open ditch bankside and sediment samples were plotted alongside curves derived from the adjacent fields for comparison. Fig. 4 illustrates isotherms derived from the Ap site A. At this site, most of the curves produced from the drain samples were steeper than those derived from the soil horizons, with the exception of 2 sampling points (end-of-pipe sample depth at outlet and base of open ditch at inlet) which produced curves that were comparable to the Ap soil horizon at this site. Although these samples were taken at 1.1 (end-of-pipe depth)

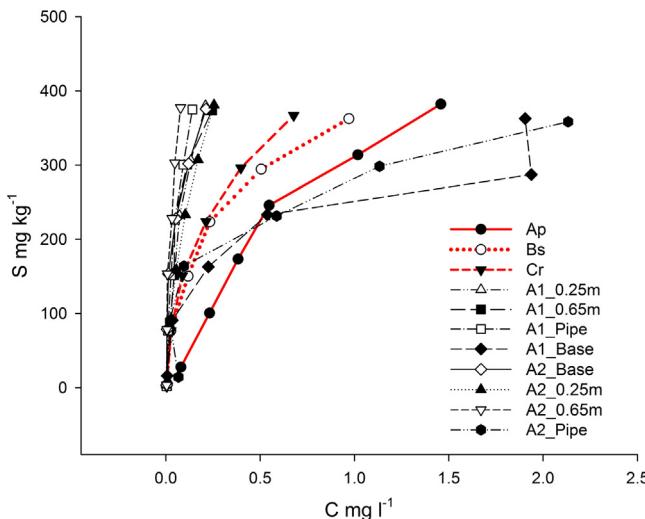


Fig. 4. Isotherm curves of P sorbed (S) plotted against final solution P concentration at equilibrium (C) of bankside and sediment ditch samples at Site A with soil horizon isotherms from the adjacent field included for comparison.

and 1.9 m (base of ditch depth) depth, the sample taken at end-of-pipe depth in the ditch could have contained topsoil that was used as backfill during drainage installation; and the sorption isotherm curves and high M3P value reflect this. Installation involved a channel being excavated along the total length of the drain first to pipe installation depth, then the 80 mm pipe was laid and a gravel pack lain down and backfilled with soil to the surface. Sorption isotherm data at Site A are presented in Table 3. The Langmuir model was fit to the data ($R^2 > 0.9$) however the fit to the Freundlich model ranged from $R^2 = 0.49$ to $R^2 = 0.91$ with the poorest fits from samples taken at end-of-pipe and base of open ditch locations. A higher range M3Al ($871\text{--}1705 \text{ mg kg}^{-1}$) values were recorded from samples taken from the open ditch and the majority of these samples also measured higher sorption values than those derived from the soil profile of the adjacent field. Readily desorbable P (WSP) values in the drain samples were lower ($0\text{--}0.44 \text{ mg kg}^{-1}$) compared to the high WSP fraction recorded in the Ap horizon perhaps an indication better sorption and binding of P in the open ditch sediment due to some higher P sorption values recorded in the ditch. Highest sorption properties were recorded in the subsoil bankside samples at the inlet and outlet and lowest PSI values recorded at end-of-pipe depth and open ditch base locations. Single point sorption indices were comparable with those values measured in the soil profile samples, and ranged from 383 to 484 mg kg^{-1} in the drainage samples.

Sorption isotherms derived from subsoil bankside and sediment samples at Site B plotted alongside field soil isotherms from the adjacent field for comparison in Fig. 5. Visual inspection of these curves indicated some similarity to those derived from the subsoil horizons at this site, with the exception of 2 sampling points at inlet at 1.7 m at end-of-pipe and open ditch base locations. These 2 drainage curves reflected the isotherm derived from the Apg horizon from the adjacent field. Sorption isotherm P characteristics similar to those recorded in the surface soil horizon at this site were found at subsurface and bankside samples in the ditch and likely due to backfilling of topsoil after the installation of artificial drains. Sorption isotherm data at Site B are presented in Table 3. The majority of the isotherms derived from drainage samples reflected those from the subsoil horizons in the adjacent field, with lower P sorption properties compared to site A, largely due to lower Al and Fe (Paultner and Sims, 2000; Daly et al., 2015). However, a higher range of WSP values were extracted from drain samples at site B ($0.16\text{--}2.75 \text{ mg kg}^{-1}$) compared to site A ($0\text{--}0.44 \text{ mg kg}^{-1}$) and is

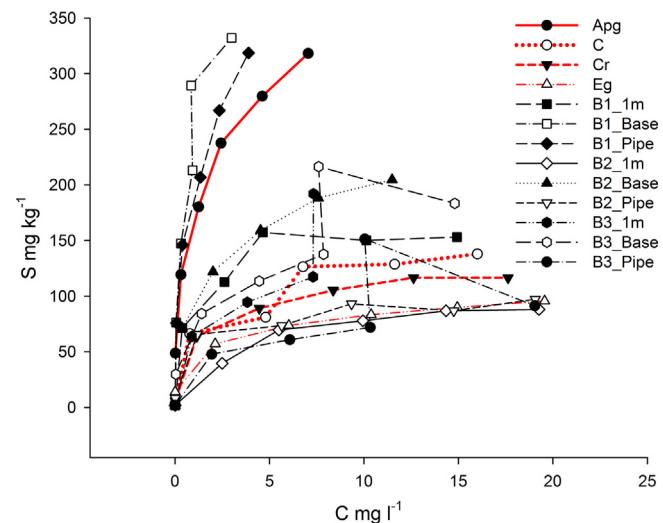


Fig. 5. Isotherm curves of P sorbed (S) plotted against final solution P concentration at equilibrium (C) of bankside and sediment ditch samples at Site B with soil horizon isotherms from the adjacent field included for comparison.

suggested here that lower retention and sorptive capacities for P entering the drainage system could be accompanied by high WSP fractions in sediment that is loosely bound, particularly evident at the base of the open ditch at B3. Langmuir parameters S_{\max} ranged from 96 to 417 mg kg^{-1} in the open ditch, comparable to the range of values derived from the soil profile ($98\text{--}333 \text{ mg kg}^{-1}$). A similar range of PSI ($38\text{--}290 \text{ mg kg}^{-1}$) and Freundlich K values ($24\text{--}264 \text{ mg kg}^{-1}$) were captured in the open ditch compared to adjacent field. Low M3Al and M3Fe values were recorded in the open ditch, similar to the soil profile values. This aligns with previous work by Shore et al., 2015 who found similarities in ditch sediment P characteristics (Al, Fe and Ca) and field soils in two agricultural watersheds.

3.4. Phosphorus concentrations in drainage water, end-of-pipe and shallow groundwater at both sites

Table 4 presents DRP, TDP, TRP, TP, PP and DUP concentration captured in the open ditch, end-of-pipe and in-field piezometers at both sites. Ditch samples refer to samples taken from A1 and A2 locations in the open ditch at site A ($0.003\text{--}0.183 \text{ mg l}^{-1}$) and B1 to B3 along the open ditch at site B ($0\text{--}0.084 \text{ mg l}^{-1}$). Over the monitoring period DRP concentrations measured along the open ditch at site A were consistently higher than site B with average values of 0.059 mg l^{-1} and 0.024 mg l^{-1} measured at site A and B, respectively. Likewise, higher TP values were recorded at Site A with an average value of 0.124 mg l^{-1} compared to 0.054 mg l^{-1} measured at Site B. Phosphorus speciation of water samples recorded higher values at Site A, although both sites recorded similar PP values. At both sites, DUP accounted for 46 and 50% of TDP whilst PP accounted for 16 and 17% at sites A and B, respectively. Site A recorded DRP values in the open ditch that could potentially contribute to P loss to nearby streams, as surface water quality monitoring under the WFD requires average annual DRP concentrations within 0.035 mg l^{-1} (or 95th percentile within a boundary value of 0.075 mg l^{-1}) in order to assign good ecological status. Along the open ditch, average DRP values exceeded the environmental quality standard (EQS) of 0.035 mg l^{-1} with 20% of samples exceeding the boundary value of 0.075 mg l^{-1} for surface water quality as provided for under the European Union Water Framework Directive (EU WFD) (OJEC, 2000). Over the sampling period, average DRP values along the open ditch at Site B were 0.019 mg l^{-1} , within the EQS for good water quality. No samples exceeded the

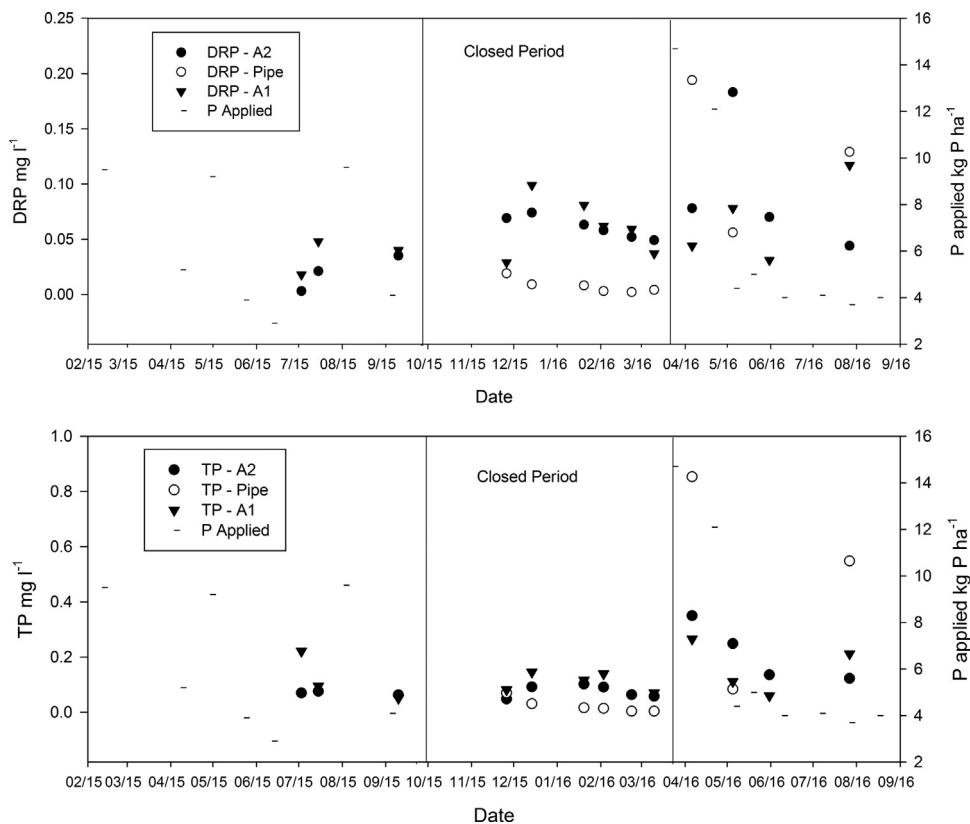


Fig. 6. Dissolved reactive phosphorus (DRP) (top) and TP (bottom) values recorded from the open ditch at locations A1 and A2 along the ditch, and end-of-pipe samples (Pipe) at Site A, with P application rates and time included outside of the 'closed period' when applications of P are restricted.

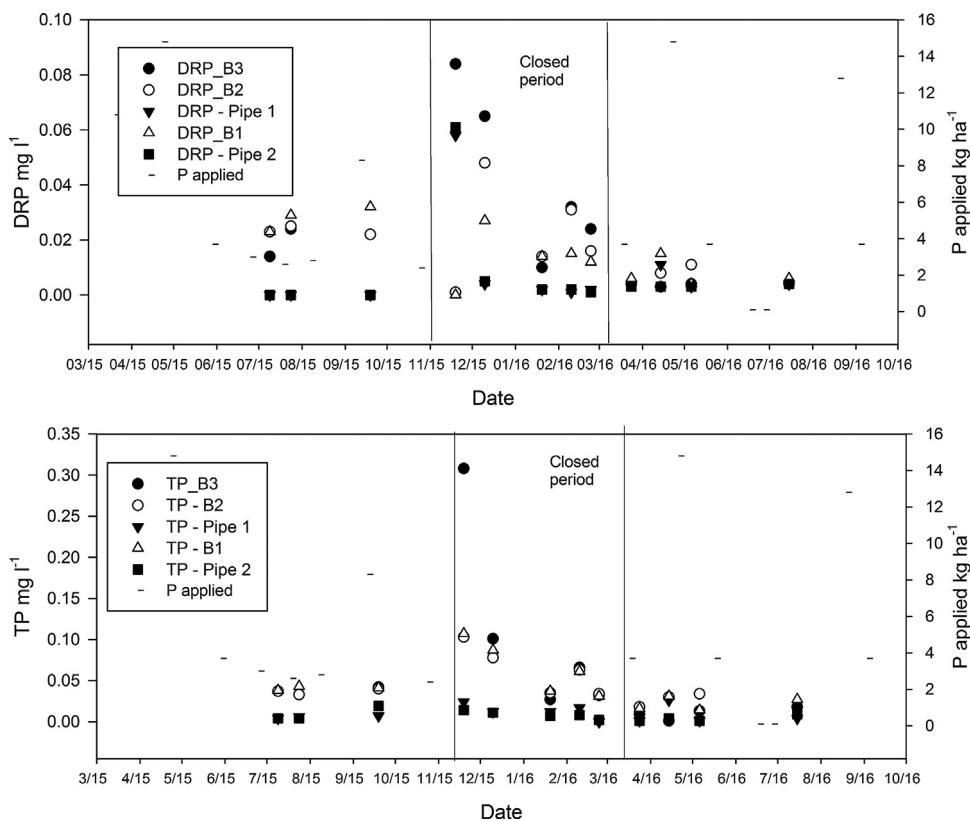


Fig. 7. Dissolved reactive phosphorus (DRP) (top) and TP (bottom) values recorded from the open ditch at locations A1 and A2 along the ditch, and end-of-pipe samples (Pipe) at Site B, with P application rates and time included outside of the 'closed period' when applications of P are restricted.

boundary value of 0.075 mg l^{-1} as provided for under the EU WFD. Similarly, the subsurface water quality at this site recorded low DRP values recorded an average value from the site of 0.009 mg l^{-1} .

Whilst both sites were not hydrologically isolated from the other fields on the farm and wider catchment area, DRP concentrations in the open ditch include losses from adjacent and nearby fields that were not included in this study but are of interest as they discharge to neighbouring water bodies. In addition, point sources on the farm such as farm yard and could potentially contribute to DRP concentrations. The presence of a highly desorbable P fraction in the Ap horizon at Site A could potentially contribute to DRP concentrations in the open ditch via surface overland flow pathways. However, given the high P sorptive properties of the subsoil bank-side and sediment samples at this site, and coupled with a low WSP fraction in the sediment, there may be potential for some mitigation of DRP losses from the adjacent field by ditch sediment. Water quality measured in the pipe at 1.1 m depth, and feeding into the open ditch, captured a higher range of TP, DRP and PP compared to samples taken from in-field piezometers at the same depth. The water samples collected from end-of-pipe locations represent the interaction of drainage water with soil biogeochemistry and is influenced by the soil biogeochemistry from a contributing zone which includes water re-directed downward from the Ap horizon and subsequent subsoil horizons above the installation depth. Whereas the piezometers on site were installed to shallow depths and typically have a much smaller zone of contribution due to low permeability subsoil. Piezometer water samples represent soil pore-water from the immediate vicinity of the screened interval of the piezometer. Lowest P concentrations were recorded in piezometer samples indicating some retention and attenuation of P by surrounding soil. Water soluble P from the Ap horizon could have contributed to P concentrations discharging into the open ditch from the end-of-pipe location, whereas at the same depth, piezometer samples indicating attenuation of P within the soil matrix at this depth. In terms of soil functions, the indications at this site are loss of water purification function at that depth due to drain installation.

3.4.1. Temporal trends in DRP and TP values and P inputs

At site A, the average daily rainfall was 5.8 mm and average daily flow rate in the open ditch channel was $472 \text{ m}^3 \text{ day}^{-1}$. Maximum values of both daily rainfall and flow rate over this period were 71 mm and $1702 \text{ m}^3 \text{ day}^{-1}$, respectively. At site B, average daily rainfall and flow were 3.6 mm and $673 \text{ m}^3 \text{ day}^{-1}$, with maximum values of rainfall and flow at this site of 29.6 mm and $2827 \text{ m}^3 \text{ day}^{-1}$. Fig. 6 presents Dissolved RP and TP concentration in the drain, pipe and in-field piezometers at Site A are plotted over the monitoring period with the timing and rates of P inputs as fertiliser and slurry P included (Fig. 6). An average DRP value of 0.047 mg l^{-1} was measured in samples collected from the end-of-pipe location at 1.1 m depth, although median values of 0.009 mg l^{-1} indicated elevated values which occurred during April and July 2016 coinciding with the presence of grazing animals and when inputs of fertiliser and slurry P occurred. Current agricultural measures restrict the spreading of manures or fertilisers during wetter winter months when the risk of nutrient transfer is greatest. This time-frame, termed here as the 'closed period' is denoted along the timeline in Figs. 6 and 7. Average DRP values in the open ditch during the closed period were 0.061 mg l^{-1} indicative of diffuse legacy P losses from the site and surrounding fields. In the months immediately following the closed period an average DRP of 0.081 mg l^{-1} was recorded, possibly due to incidental losses with potential losses from cow traffic on farm roadways, however these observations are based on a small number of samples which limits our ability to establish a clear signal from incidental losses at this site. At Site B average DRP values

of 0.024 mg l^{-1} were recorded during the closed period and for samples taken outside of the closed period.

3.5. Field and open ditch P dynamics and Implications for remediation of drainage P losses and drainage design

Christianson et al. (2016) highlighted the importance of additional field scale studies and data on soil properties to develop a more comprehensive understanding of P loss in drainage waters. Our study has shown that collecting soil biogeochemical data at surface and subsurface depths at in-field and open ditch locations during the site investigation phase of land drainage design could identify sorptive and desorptive properties within the soil profile of potential drainage sites. Although many drainage models use nutrient loadings (Christianson and Harmel, 2015; Dang et al., 2010) EU WFD member states are required to monitor average annual in-stream DRP concentrations as physico-chemical criteria for assigning good water quality and ecological status. Despite high P sorption capacity within the humic surface horizon at site A previous work on high OM soils (Guppy et al., 2005; Daly et al., 2001) identified competition between OM and P for sorption sites resulting in high soluble P concentrations in the soil solution. Although TP and high P sorption capacity was measured in this horizon a high proportion of this was not fixed but readily desorbable, as evidenced by the elevated WSP fraction. In contrast, the subsurface horizons in the same field exhibited high sorption capacities that increased with depth (due to leaching of Al and Fe) and were accompanied by lower extractable and soluble forms of soil P. This is further evidenced by low concentrations of DRP measured from in-field piezometer samples which recorded a mean value of 0.003 mg l^{-1} over the sampling period. This site could be biogeochemically characterised with a highly desorbable P fraction at the surface and high P retention or attenuation capacity in the subsurface horizons. Adjacent to this field, DRP concentrations in the open ditch were higher than the EQS, particularly during periods when fertiliser and slurry were spread on the site and cows were grazing out on this land. High P sorption was evident in the ditch which could mitigate some of these losses.

Over time, the installation of tile drainage is designed to reduce surface overland flow, specifically, spikes or peaks in overland flow during intense storm events (Christianson and Harmel, 2015). A change in flow regime at Site A could reduce surface DRP concentrations as water is redirected from a P mobilising layer toward a P attenuating one. Further remediation along the open ditch network such as dredging along the open ditch that could expose subsurface soil with high sorption capacities could be an option if losses continue to occur thereafter. However, before immediate engineered solutions such as reactive media structures (Allred, 2010; Allred and Racharaks, 2014) or dredging (Shore et al., 2015) is proposed for any site, it is potentially more cost effective to characterise the P chemistry within the open ditch first. For example, our results have demonstrated that P sorption characteristics along an open ditch mostly reflect the subsurface soil horizons of nearby or adjacent field soils, with some mixing of topsoil at locations where backfilling of tile drains has occurred during installation. This finding has implications for how drainage measures are selected and a measure such as dredging to expose new sites for P sorption and attenuation would not be appropriate for Site B in our study but could potentially remediate high drainage water P concentrations at Site A, largely owing to the nature of the P isotherms along the open ditch and in the sediment. For sites similar to Site B in this study, with low P sorption in the ditch sediment a potential measure could include incorporating high P sorbing topsoil/backfill (with higher P sorption) into the cover ditch sediment and increase the potential for P sorption

in the ditch. This could be viewed as analogous to P removal by the addition of high P sorbing materials (Penn et al., 2007; Allred and Racharaks, 2014) except using the natural attenuation of Al and Fe in soil, provided these properties are known. Furthermore, subsurface horizons P sorption and desorption properties have implications for the depth and spacing of artificial drains, especially if water is redirected toward a low P sorbing layer in the soil profile.

4. Conclusions

This study examined soil, sediment and water P chemistry at two poorly drained field sites under permanent grassland with similar P fertiliser management regimes and land use. In-field tile drains were installed at each site in 2013, adjacent to an open ditch network. Both sites exhibited contrasting soil P chemistries, within and between sites. The soil type at site A was described as a Humic Brown Podzolic and the P chemistry was dominated by high TP and a large fraction of readily desorbable P in the surface horizon despite its high P sorption capacity. Within the same site, and in contrast, subsurface horizons had high amounts of leached Al and Fe, high P sorption, and low desorbable P. DRP concentrations were monitored in the open ditch, end-of-pipe and in-field piezometers and highest values were recorded in the open ditch ($0.03\text{--}0.183\text{ mg l}^{-1}$) at Site A, potentially due to a diffuse and point sources on the farm and surrounding area, with maximum values occurring when animals were present and during periods when fertiliser and slurry P was spread on the adjacent field source at the surface. Higher P concentrations were recorded at end-of-pipe locations compared to piezometers at similar depth, and attributed to a larger contributing area reaching the pipe from the surface and surrounding subsurface layer. Phosphorus was attenuated or sparingly soluble in subsurface soil horizons rich in Al and as evidenced by low piezometer DRP values. The P chemistry of banksides and sediment samples taken from the open ditch show reflected the sorption properties of subsurface soil horizons. At Site A higher sorption capacities and lower desorbable P was measured in the ditch compared to the adjacent field site indicating some potential to act as a sink for DRP in the overlying drainage water. In contrast, Site B was described as having a moderate P sorption capacity at the surface horizon but very low P sorption capacity in subsurface horizons largely due to high% sand and low Al and Fe contents providing limited sites for P sorption to occur. This site was characterised by low soil P and low drainage water DRP and TP values.

Contrasting surface and subsurface soil chemistries has implications for P management drainage design and drainage measures. Sites with a high soluble P fraction at the surface but potentially buffered and attenuated by subsurface P sorption, require drainage designed to a depth that redirects water vertically towards the attenuating layer. Recording the depth and chemical nature of soil horizons will inform the depth at which drains can be installed so that they coincide with an attenuating layer. Furthermore, soil and drainage biogeochemical information will also inform whether drainage measures such as dredging are appropriate and likely to expose sediment that has the capacity to attenuate P from overlying water. This measure would be unsuitable in scenarios similar to Site B in our study, where P sorption decreased with soil depth and low P sorption values are recorded in the drainage sediment similar to subsurface field soil. In situations where P mitigation was required under similar soil and sediment P properties, dredging could be counterproductive, but perhaps adding topsoil with high P sorption into the ditch could enhance P sorption. The 'right measure, right place' approach to drainage measures should include an assessment of sediment P properties before implementation.

Acknowledgements

The authors wish to thank the farmers for allowing access to their field sites and acknowledge the support and funding of Teagasc for this research. The authors thank Mr. Denis Brennan and Ms. Maria Pettitt for laboratory analysis of water samples; Ms. Linda Moloney Finn for ICP-OES analysis of soil digest; Dr. Brian Reidy for soil survey and profile descriptions and Mr. Simon Leach for GIS support and map production.

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