

Research article

Impact of P inputs on source-sink P dynamics of sediment along an agricultural ditch network

G. Ezzati^{a,b}, O. Fenton^a, M.G. Healy^b, L. Christianson^c, G.W. Feyereisen^d, S. Thornton^e, Q. Chen^f, B. Fan^f, J. Ding^f, K. Daly^{a,*}^a Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland^b Civil Engineering, College of Science and Engineering, Ryan Institute, National University of Ireland, Galway, Galway, Ireland^c Department of Crop Sciences, University of Illinois at Urbana-Champaign, Urbana, IL, USA^d USDA-Agricultural Research Service (ARS), St. Paul, MN, USA^e Groundwater Protection and Restoration Group, Krotto Research Institute, University of Sheffield, Sheffield, United Kingdom^f Beijing Key Laboratory of Farmyard Soil Pollution Prevention-control and Remediation; College of Resource and Environmental Sciences, China Agricultural University, Beijing, 100193, PR China

ARTICLE INFO

Keywords:

Drainage water
Farm pollution
Phosphorus
Soil
Agriculture
Sediment

ABSTRACT

Phosphorus (P) loss from intensive dairy farms is a pressure on water quality in agricultural catchments. At farm scale, P sources can enter in-field drains and open ditches, resulting in transfer along ditch networks and delivery into nearby streams. Open ditches could be a potential location for P mitigation if the right location was identified, depending on P sources entering the ditch and the source-sink dynamics at the sediment-water interface. The objective of this study was to identify the right location along a ditch to mitigate P losses on an intensive dairy farm. High spatial resolution grab samples for water quality, along with sediment and bankside samples, were collected along an open ditch network to characterise the P dynamics within the ditch. Phosphorus inputs to the ditch adversely affected water quality, and a step change in P concentrations (increase in mean dissolved reactive phosphorus (DRP) from 0.054 to 0.228 mg L⁻¹) midway along the section of the ditch sampled, signalled the influence of a point source entering the ditch. Phosphorus inputs altered sediment P sorption properties as P accumulated along the length of the ditch. Accumulation of bankside and sediment labile extractable P, Mehlich 3 P (M3P) (from 13 to 97 mg kg⁻¹) resulted in a decrease in P binding energies (k) to < 1 L mg⁻¹ at downstream points and raised the equilibrium P concentrations (EPC₀) from 0.07 to 4.61 mg L⁻¹ along the ditch. The increase in EPC₀ was in line with increasing dissolved and total P in water, demonstrating the role of sediment downstream in this ditch as a secondary source of P to water. Implementation of intervention measures are needed to both mitigate P loss and remediate sediment to restore the sink properties. In-ditch measures need to account for a physicochemical lag time before improvements in water quality will be observed.

1. Introduction

Diffuse and point-source inputs from agriculture result in degradation of water quality (Sutton et al., 2009), including loss of aquatic biodiversity (FAO, 2011) and ecosystem services (Schindler et al., 2010). Incidental and legacy P losses from agriculture to water (Haygarth et al., 2005) are major sources which contribute to eutrophication (Verheyen et al., 2015). The European Union Water Framework Directives (OJEC, 2000) requires member states to achieve at least “good” status in all water bodies and implement “programmes of measures” to minimise point and diffuse P losses (Kronvang et al., 2007; Sharpley,

2016; Macintosh et al., 2018; Melland et al., 2018). In Ireland the Nitrates Directive regulates P use on farms as a baseline measure to protect water bodies from nutrient and sediment loss. However, legacy P stores which are stored over decades of excessive P applications are difficult to mitigate and further measures may be needed before any impact on water quality is observed (Sharpley et al., 2013; Vadas et al., 2005; Fiorellino et al., 2017). Typically, water infiltrates into soil and interacts with legacy P stores along the transfer continuum. This water often discharges to drainage ditches acting as corridors for nutrient movement (Needelman et al., 2007). However, concentrations of dissolved P in these networks can vary due to direct discharges from pipes connected

* Corresponding author.

E-mail address: karen.daly@teagasc.ie (K. Daly).<https://doi.org/10.1016/j.jenvman.2019.109988>

Received 23 September 2019; Received in revised form 2 December 2019; Accepted 11 December 2019

Available online 19 December 2019

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with a source, or as a result of sediment chemistry (Moloney et al., 2020).

Clagnan et al. (2019) examined the connectivity of surplus nutrients lost from an intensive dairy system to adjoining ditch networks and found elevated DRP in drainage water. Moloney et al. (2020) classified the on-farm ditch networks according to P loss risk and concluded that the highest risk was attributed to connectivity of the farm yards to ditches in combination with legacy P stored in the sediment. There is a constant interplay between dissolved P in water and bankside-sediment/sediment chemistry in which physiochemical properties such as aluminium (Al), iron (Fe), calcium (Ca), clay, pH and organic matter (OM) can enable mobilisation or immobilisation of P along the transfer continuum (Thomas et al., 2016). Shore et al., 2016 classified drainage ditch networks based on physical and chemical attributes and highlighted the role of vegetation for nutrient and water attenuation along the networks (Haggard et al., 2004; Smith et al., 2005). The challenge for catchment managers and water policy is identifying the locations where these measures should be implemented. Ditch bank side soil and sediments have a foundation in the retention and mobilisation of P along these networks (Daly et al., 2017; Delgado and Berry, 2008; Dollinger et al., 2015; Daly et al., 2017; Fenton et al., 2017). Daly et al. (2017) found that subsurface horizons rich in Al could attenuate P or make it less soluble and concluded that a 'right measure, right place' approach to drainage measure implementation could be effective. However, Haggard et al. (2004) reported that sediments are spatially heterogeneous and can act as temporary stores of P or a transient storage pool that may be released back into water depending on *in situ* conditions. This transient nature of sediment P can influence the ditch capacity to become a source, sink or regulator of DRP in ditch water (Smith et al., 2005). Hence, characterisation of ditch networks and closer monitoring of mobilisation of P is important in terms of their influence on the potential for nutrient losses to water (Kurz et al., 2005) and ditch management.

There is a lack of basic understanding of how a ditch network functions as both mobilisers and an attenuators of nutrients area both laterally and vertically and how this might change along the network. The primary objective of the current study was to identify optimal locations for implementing mitigation measures along an agricultural ditch, by considering the source-sink dynamics for P. Spatial variation in bankside soil and sediment P properties were measured along a ditch connected to an intensive dairy farm, and coupled with spatial and temporal DRP trends in the drainage water. The connectivity between surface (runoff) and subsurface (groundwater and artificial drainage system) flow pathways was established. An intensive dairy farm located in Southeast Ireland was chosen as a case-study site for this work. The catchment draining the farm was delineated and the main ditch carrying water from the farm to an outlet point provided the location for soil and sediment sampling and monitoring of water quality on the farm. Along this ditch, bankside soil and sediment samples were taken at locations and characterised for their P sorptive properties and P source/sink dynamics. Water quality draining the ditch was monitored for soluble, particulate and total P fractions over an 18 month period to profile P concentrations in the overlying water in the ditch so that a location for a potential mitigation option could be identified.

2. Materials and methods

2.1. Site description and identification of sampling locations

The Johnstown Castle catchment, delineated in Fig. 1, contains an intensive dairy farm (190.4 ha) located in SE Ireland in North Atlantic Europe (52°17'52" N and 06°29'48" W). The 30-year mean annual rainfall on this site is approximately 1000 mm, of which approximately half is drained at different rates into well to poorly drained soils (Fig. 1). Due to its glaciated origins, soils at the site are heterogeneous, varying in drainage class from well to poorly drained soils (saturated hydraulic

conductivity ranges from 0.0001 to 0.029 m d⁻¹ (Jahangir et al., 2013)). The grassland areas of the site consists of poorly and imperfectly drained Gleys to well drained silty clay loam (topsoil) and dense gravels inter-mixed with clay at 0.6–10.0 m subsoil geology. In poorly drained areas, an artificial drainage system has been installed and in-field drains discharge to a ditch network with high connectivity to the surrounding landscape (Fig. 2). A detailed description of the drainage network is provided in Clagnan et al. (2019). The total length of the drainage system within the catchment boundary is 10.25 km, comprising of 1.01 km of ditches with drains installed at approximately 1.2–2.9 m depth. The main ditch within the farm runs parallel to the farmyard and is 850 m in length. This ditch starts with shallow depth of 30 cm and gradually gets deeper to 270 cm, with 20 m above ordnance datum (AOD) change in elevation, and is the focus of this current study.

In terms of runoff and sub-surface drainage, an area of 94 ha (Kurz et al., 2005) – delineated up-gradient (24 ha) and down-gradient (70 ha) in Fig. 1 – contributes to discharge which enters the ditch through concrete pipes at No 1 & 2 (Fig. 2). The down-gradient contribution area enters the ditch at No 2 and is represented by the sampling point A. The up-gradient area (Fig. 1) enters the ditch at No 1. Other sources of water into the ditch stem from direct rainfall or groundwater. A groundwater well between the ditch and the farmyard (Fig. 2, Well 2 total depth of ~5 m below ground level (bgl)) indicates an average water table height of <1 m bgl with a hydraulic gradient of 0.5, indicating discharge to the ditch through the bankside subsoil horizons and through the base of the ditch. Fig. 2 shows the groundwater elevation in the area of the ditch with contour beside the farm yard running perpendicular to the flow of the ditch. This places the water-table at 1 m below the farmyard which interacts with the depth of the concrete slurry storage facilities. On the opposite side of the ditch poorly drained soils have not been artificially drained and are presently out of production. Based on their connectivity and landscape position, Moloney et al. (2020) identified agricultural ditches as being high risk areas of P loss on Irish farms. At the Johnstown Castle, water quality and P dynamics of bankside and sediment samples along the length of the ditch were collected to provide a detailed appraisal of the impacts of sources entering the ditch. Seven sediment and water sampling points (Locations A, B, C, D, E, F, G in Fig. 2) along the ditch network were selected for sample collection.

2.2. Bankside and sediment sampling and analysis

Sediment samples from the bankside and base locations of the ditch were collected in October 2017. Grass and plants were removed and the bankside profile was sampled at depth intervals of 30 cm from top to base. The number of samples collected at each sampling points varied according to the depth of the ditch along the total length and are listed as follows: A: 1; B: 3; C: 4; D: 4; E: 8; F: 10; G: 9. Location-Code represents the depth interval number (e.g. A1) as shown in Tables 2 and 3. Similarly, sediments from the base of the ditch were collected, at the same location as bankside samples.

2.2.1. Soil chemistry analysis

All sediment samples were oven dried (40 °C) and sieved (2 mm) to remove stones and debris, and stored at room temperature prior to analysis. Sediment pH was analysed on 2:1 soil-water ratio paste and OM was measured based on loss-on-ignition of 4 g of samples at 500 °C (Schulte, 1995). The modified Mehlich 3-P (M3P) method (Mehlich, 1984) was used to determine labile extractable P, Al, Fe, Ca using a soil solution ratio of 1:10 in Mehlich 3 reagent (0.2 M CH₃COOH + 0.25MNH₄NO₃ + 0.015 M NH₄F + 0.13 M HNO₃ + 0.001 M EDTA). Two gram samples were shaken on a reciprocating shaker for 5 min and the supernatant was filtered to determine concentrations of labile extractable P, Al, Fe and Ca.

2.2.2. Phosphorus sorption isotherm and equilibrium P concentration

The P sorption properties of the bankside and sediment samples were

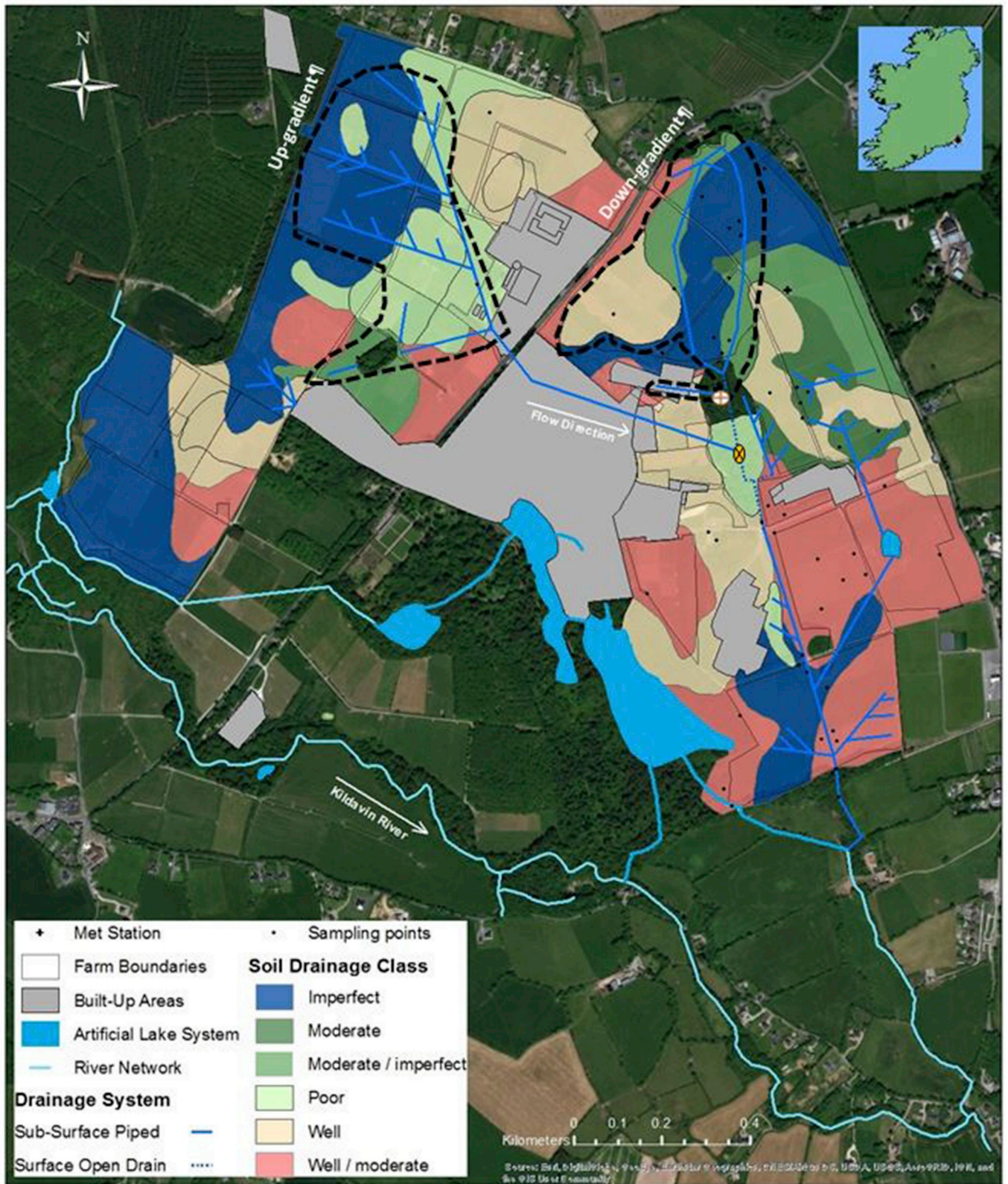


Fig. 1. Johnstown Castle Intensive Dairy farm showing the up-gradient and down-gradient surface/subsurface drainage system and runoff areas and their entry point into the open ditch system, soil drainage class, and sampling points across the farm documented by Kurz et al. (2005) and Clagnan et al. (2019). ● No.1; ⊕ No.2.

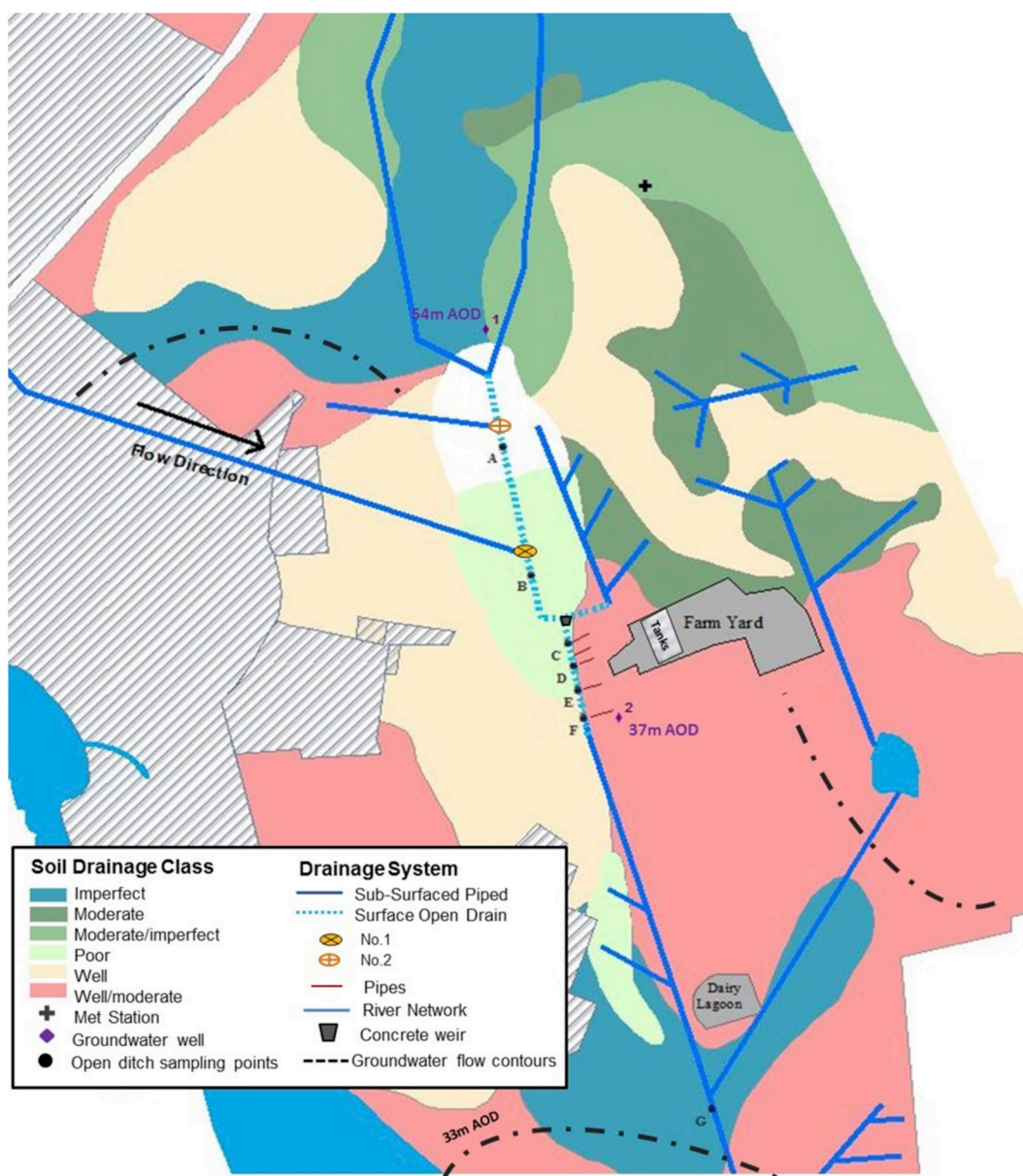


Fig. 2. In ditch grab water and soil-subsoil-sediment sampling points (Locations A-G). Position of farmyard, entry points of up-gradient and down-gradient discharge to the ditch (⊗ No.1; ⊕ No.2), position of pipes discharging directly into the ditch and water table height (m AOD) around the ditch network. Groundwater flow is perpendicular to groundwater contours i.e. into ditch.

described by a P sorption isotherm derived for all locations and depths along the ditch. Sediment samples from the bankside and base locations were equilibrated with six solutions with concentrations of 0, 5, 10, 15, 20 and 25 mg P L⁻¹ (Paulter and Sims, 2000). Analyses were carried out in duplicate by adding 30 ml of initial P solutions to 2 g sediment in 50 ml centrifuge tubes. The tubes were shaken on an end over end shaker at room temperature for 24 h, centrifuged and filtered, and the final concentration of P in solution was measured colorimetrically. The difference between initial concentration and final equilibrium P concentration (C) was calculated as P sorbed to the soil (S). The linear form of the Langmuir isotherm equation ($C/S = 1/S_{max} * k + C/S_{max}$) was fitted to the sorption data and was used to derive the maximum sorption capacity (S_{max} ; mg kg⁻¹) and k (L mg⁻¹), the constants related to the P binding energy in sediment.

The P sink/source dynamics of bankside and sediment samples was described the EPC₀ which represents a solution P concentration at the sediment-water interface where P is neither sorbed nor released. This

parameter is often used to describe the role of sediment in freshwater systems in regulating P concentrations where sediment will adsorb/desorb P in order to reach a target P concentration at equilibrium, or EPC₀. If EPC₀ measured in sediment is higher than freshwater DRP, the sediment will release P to the water column in order to reach that equilibrium solution P concentration. If the sediment EPC₀ is lower than surrounding DRP, this favours net P adsorption from water into sediment in an effort to maintain a lower P concentration in solution at equilibrium (McDowell and Monaghan, 2015). The EPC₀ in bankside and sediment samples collected along the ditch was measured using 1 g sediment equilibrated with 20 ml of solution P concentration of 0, 0.1, 0.25, 0.5, 1 mg L⁻¹ and shaken at room temperature for 24 h, centrifuged and filtered through 0.45 μm filters to measure the concentration of P in solution measured colorimetrically (Murphy and Riley, 1962). The EPC₀ was calculated from the slope of the linear plot of P sorbed on the solid phase against final solution P concentration.

2.2.3. Data treatment

Statistical analyses were carried out using R-Programming Language. The Null-hypothesis for all tests was considered to have no variance and no difference between groups and p-value of 0.05 was used to accept or reject hypothesis.

2.3. Ditch water sampling and analysis

Grab water samples from sampling points A to G (Fig. 2) were collected from Jan 2017 to July 2018. Filtered (0.45 µm) water samples were collected in 50 ml tubes and analysed for DRP using colorimetric analysis (Aquachem600 Labmedics Analytics, Thermo Clinical Labsystems, Finland) and digested with acid persulphate to determine total dissolved P (TDP). Unfiltered samples were analysed for total reactive P (TRP) using colorimetry (Aquachem) and particulate P (PP) was calculated by subtracting total dissolved phosphorus (TDP) from total phosphorus (TP). Additionally, ditch water at each location was pumped to a flow cell connected with an *in-situ* Multiparameter Probe (In Situ Inc. Ltd., USA) to measure temperature, electrical conductivity (EC), rugged dissolved oxygen (RDO), and pH under steady-state conditions.

3. Results and discussion

3.1. Trends in water quality along an open ditch

Table 1 presents summary statistics of DRP, TP, PP, and TRP across sampling points for the sample period January 2017 to July 2018. The distribution of these data is shown as boxplots in Fig. 3. Values of DRP and TP at sample points A to C were lower in comparison to values recorded further downstream from D to G. Average DRP and TP values

between A and C were 0.042 and 0.168 mg L⁻¹, respectively and increased to 0.237 mg DRP L⁻¹ and 0.48 mg TP L⁻¹ between D and G. A step change in P concentrations was observed at sample point D indicating a point source contribution possibly due to inputs from the farmyard (Fig. 2) located between sampling points D and E. Field work during the present study identified several pipes directly discharging (odorous) into the ditch from the farmyard area and these were also tested when running water discharged from the pipes and recorded DRP concentrations ranging from 0.011 to 0.093 mg L⁻¹ and TP ranging from 0.027 to 1.72 mg L⁻¹ (red straight lines between farmyard and ditch in Fig. 2). The results at point E are indicative of direct discharges from the farm yard as evidenced by maximum DRP and TP of 2.976 mg L⁻¹ and 4.89 mg L⁻¹ respectively. Downstream from D, these parameters remained high and increased along the length of the ditch with highest mean DRP at F (0.434 mg L⁻¹) almost 10 times higher than A and twice that recorded at E. Max DRP values recorded at F of 1.258 mg L⁻¹, suggested that high P inputs are not attenuated by bankside and sediment along the ditch but continued to increase downstream at G, were some extreme values were recorded, reaching maximum DRP almost twice than F. Highest values at G are likely due to the direct discharges into the ditch from the yard (positioned at 37 m AOD) along with inputs from another ditch and potentially the diffuse inputs coming from surrounding fields including a dairy lagoon, which are accumulated down slope (33 m AOD). A step-change in TP values was also observed at D. Maximum TP of between 0.11 and 0.33 mg L⁻¹ between A-C, rose to 1.32–4.89 mg L⁻¹ from D to G and these values align with previously reported TP values in agricultural ditches with a direct connection to a farmyard (Harrison et al., 2019; Moloney et al., 2020). At catchment scale, Harrison et al. (2019) reported mean TP values > 1.5 mg L⁻¹ in a riparian survey of ditches connected to farmyards and Moloney et al.,

Table 1

Summary statistics of ditch water phosphorus (P) fractions and hydrochemistry at sample points A-G along the length of ditch during January 2017–July 2018.

Location	Sample size	DRP mg L ⁻¹	TP	PP	TRP	pH	Temp. °C	EC µS cm ⁻¹	RDO mg L ⁻¹
Site A	10								
Max		0.120	0.227	0.227	0.052	8.44	12.99	471.1	10.67
Min		0.020	0.014	0.004	0.021	6.86	8.06	251.9	9.12
Mean		0.041	0.080	0.077	0.037	7.26	9.873	364.1333	9.99
Median		0.030	0.053	0.042	0.038				
Site B	10								
Max		0.088	0.110	0.110	0.093	7.27	10.07	388.8	9.64
Min		0.008	0.009	0.009	0.019	5.95	9.03	366.9	8.93
Mean		0.036	0.051	0.031	0.043	6.82	9.3	375.3	9.24
Median		0.019	0.053	0.013	0.040				
Site C	18								
Max		0.114	0.330	0.284	0.090	8.2	12.58	426.7	12.56
Min		0.021	0.028	0.005	0.025	6.97	7.92	236.7	8.21
Mean		0.054	0.087	0.066	0.045	7.23	9.625	348.5	10.18
Median		0.043	0.055	0.040	0.039				
Site D	10								
Max		0.610	2.290	0.318	1.210	7.56	12.6	423.8	10.75
Min		0.047	0.031	0.005	0.048	6.9	9.16	342	8.98
Mean		0.228	0.536	0.135	0.363	7.183	11.31	392.9	9.86
Median		0.123	0.156	0.100	0.132				
Site E	16								
Max		2.976	4.890	0.180	2.980	8.6	14.93	720	11.7
Min		0.008	0.017	0.001	0.007	6.34	7.99	252	8.89
Mean		0.272	0.536	0.036	0.432	7.32	11.14	466.1	10.28
Median		0.031	0.086	0.010	0.071				
Site F	18								
Max		1.258	1.320	0.784	1.230	8.6	14.88	560.8	10.86
Min		0.027	0.034	0.003	0.025	7.05	9.15	346.2	9.98
Mean		0.434	0.537	0.096	0.451	7.56	11.58	423.2	10.56
Median		0.147	0.165	0.058	0.167				
Site G	18								
Max		2.759	4.290	0.234	2.781	9.24	12.61	632.1	11.9
Min		0.004	0.016	0.000	0.025	6.98	8.22	233.2	8.09
Mean		0.220	0.242	0.037	0.225	7.90	9.51	385.06	10.102
Median		0.062	0.105	0.005	0.094				

Temp: Temperature; EC: Electric conductivity; RDO: Rugged dissolved oxygen. DRP: dissolved reactive phosphorus. TP: total P. PP: particulate P. TRP: total reactive P.

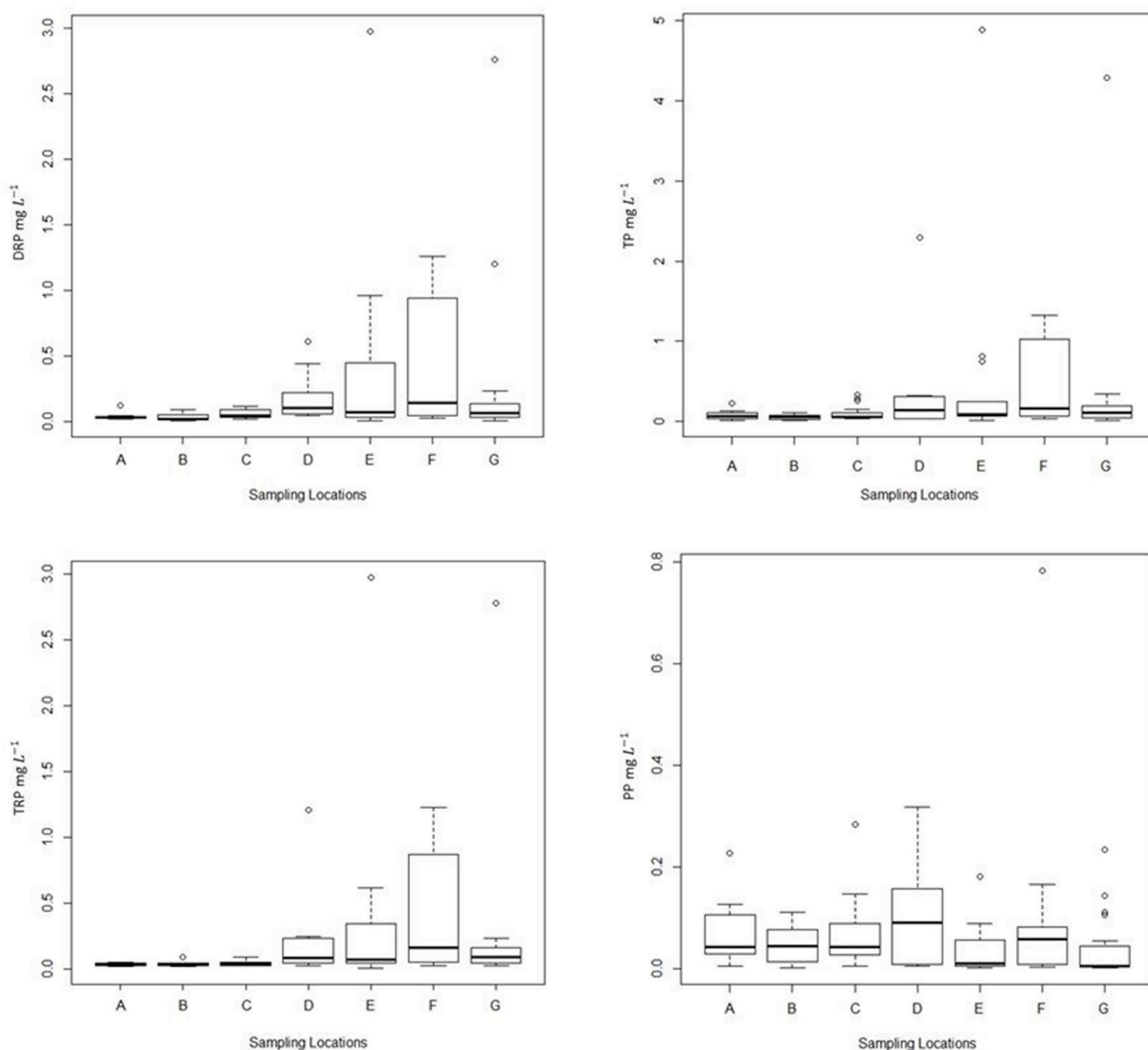


Fig. 3. Boxplots showing distribution of water quality data: DRP, TP, PP, and TRP (mg/L) at sampling locations A-G. The midline represents the median.

(2020) have identified this type of ditch as highest risk for P loss, if its landscape position allows for a direct connection into watercourses, compared to disconnected and secondary ditches.

Over the length of the ditch, average PP values were similar at all sample points except D, where a sharp increase to 0.135 mg L^{-1} was observed, coinciding with potential point source inputs from the farmyard. However, mean PP values further downstream fell back to within the range observed at upstream points, indicating some attenuation of the particulate fraction from this point onward. Point source inputs to the ditch were evident at sample point D, as soluble P remained high along the length of the ditch. However, the sharp increase in PP reverted to lower concentrations, indicating some ability to attenuate particulate fractions downstream.

3.2. Bankside and sediment characteristics

The biogeochemical properties of bankside and sediment samples for each depth interval are represented by Mehlich extractable Al, Fe, Ca, % OM and pH, and are presented in Table 2. Sediment and bankside pH ranged from 5.38 to 7.9, with high pH values coinciding with highest

values of Ca at sample points E, F and G. In general, most of the bankside and sediment samples had a neutral pH and moderately low Al and Fe values compared to those recorded in previous studies on Irish soils and sediments (Daly et al., 2015, 2017). High extractable Ca was evident at sample points E, F and G, perhaps as a consequence of a change in soil characteristics or soil type along this reach of the ditch as illustrated in Fig. 2. The % OM ranged from 1.8 to 21.3% from point A to G, demonstrating the variability in soil types and drainage classes on surrounding fields at the site, with highest values recorded at surface bankside samples on imperfectly drained soils and lowest values along the length of the ditch dominated by well drained soils (Fig. 2).

Extractable metals Al, Fe and Ca have been reported to have a high affinity for P in both soils and sediment (Gächter and Müller, 2003; Mellander et al., 2012; Daly et al., 2017). However, the bankside/sediment analysis of our study showed low level of Al (range of 355 mg kg^{-1} between bankside of all locations) and Fe (range of 351 mg kg^{-1} between all locations except C4 which showed sharp increase to 781 mg kg^{-1}), with moderate to high M3Ca values (range of 4223 mg kg^{-1} with lowest values recorded at D and highest at G in the imperfectly drained area of the farm).

Table 2

Bankside and sediment physico-chemical properties Mehlich extractable Al, Fe and Ca, % organic matter (OM) and pH from bankside samples at 30 cm each depth intervals and sediment at the base of the ditch, taken at sample points A to G along the length of ditch.

Location	Depth	pH	OM	M3Ca	M3Al	M3Fe
Code	(cm)		(%)	mg kg ⁻¹		
Site A						
A1	0–30	6.9	3.2	12,568	213	230
Sediment		6.0	1.8	977	259	134
Site B						
B1	0–30	5.38	8.0	12,363	448	259
B2	30–60	5.42	5.5	10,592	511	308
B3	60–100	5.66	5.0	1172	449	401
Sediment		7.2	3.1	1530	173	26
Site C						
C1	0–30	6.1	6.8	1811	338	284
C2	30–60	6.2	4.8	15,012	309	269
C3	60–90	7.3	2.8	14,563	234	418
C4	90–110	7.5	5.2	34,854	65	781
Sediment		7.9	1.0	698	68	139
Site D						
D1	0–30	6.5	5.2	1996	469	149
D2	30–60	6.5	2.0	792	362	67
D3	60–90	6.4	0.8	303	130	142
D4	90–110	6.7	1.7	870	205	323
Sediment		7.8	1.4	986	91.88	190
Site E						
E1	0–30	7.1	5.6	25,454	180	264
E2	30–60	7.2	6.1	21,864	200	276
E3	60–90	7.4	5.0	22,672	285	193
E4	90–120	7.4	3.9	19,943	373	215
E5	120–150	7.5	2.9	13,851	411	178
E6	150–180	7.6	1.4	849	256	236
E7	180–210	7.9	2.4	20,217	369	146
E8	210–240	7.9	1.0	20,175	362	154
Sediment		7.8	2.9	91	89.54	239
Site F						
F1	0–30	6.8	4.6	19,997	493	225
F2	30–60	5.9	4.4	1397	399	230
F3	60–90	6.0	3.9	12,546	456	226
F4	90–120	6.2	3.8	12,148	277	164
F5	120–150	6.0	3.8	11,765	328	179
F6	150–180	6.1	3.2	11,054	191	157
F7	180–210	6.4	5.7	17,744	307	278
F8	210–240	6.6	7.1	22,538	343	245
F9	240–270	6.7	7.4	26,862	484	266
F10	270–290	6.7	6.1	23,473	476	191
Sediment		7.2	3.3	1705	158.73	336
Site G						
G1	0–30	6.3	21.3	45,266	376	261
G2	30–60	6.5	18.1	38,003	312	226
G3	60–90	6.6	17.7	42,736	372	280
G4	90–120	7.1	6.5	2728	399	275
G5	120–150	6.7	10.1	25,664	315	260
G6	150–180	7.1	8.0	27,634	251	225
G7	180–210	7.1	5.4	19,883	256	282
G8	210–240	7.4	17.7	18,495	244	266
G9	240–270	7.8	1.3	15,364	129	204
Sediment		7.6	1.5	1015	143.4	266

3.3. Trends in Bankside and sediment P dynamics along the ditch network

Mehlich3 extractable P varied along the length and depth of the ditch network, with values exceeding the agronomic optimum of 50 mg kg⁻¹ recorded at all sample points except A and C. Value in Table 3 indicate a shift toward higher M3P values at E which continued downstream reaching highest M3P values recorded at the surface bankside samples at G of 101–108 mg kg⁻¹ at depth of 90 cm. The step change in water quality P values recorded at D, signalling point source inputs, was also observed in bankside and sediment P data; however, this occurred at the next downstream sample point (E). Welch's *t*-test results showed significant differences in M3P and EPC₀ values from D to E (p-value < 0.05) and D and G (p-value of 0.0084), and significant differences in EPC₀

values between B and G (p-value = 0.009). This implies that whilst point source P impacted water quality at D, these inputs may be mobilised downstream where they start to accumulate as M3P in sediment, starting at E. At upstream points between A and C, M3P values were generally low; however, accumulation of extractable P is evidenced by increasing M3P values from E, downstream to G and likely due to P deposition by water draining the site. Box plots in Fig. 4 illustrate the shift upwards in extractable P along the length of the ditch.

Phosphorus sorption isotherm parameters S_{max} and *k* representing sorption capacity and P binding energies are presented alongside EPC₀ along the length and depth of the ditch in Table 3 with the spread of data represented as boxplots in Fig. 4. Values of *k* ranged from 0.3 to 2.9 L mg⁻¹ with lowest values recorded at sample point G and coinciding with high M3P values at this point. This parameter, representing P binding and affinity, decreased along the length of the ditch, from point E onward, and coincided with the upward shift in extractable P bankside and sediment samples from E to G. Bankside and sediment locations downstream were characterised by loosely bound P and high extractable P, thereby increasing the likelihood of P loss to the overlying water. The EPC₀ parameter in this study was measured along the length and depth of the ditch to identify whether this ditch acts as a source or sink at bankside and sediment locations along its reach. However, EPC₀ illustrated in Fig. 4 and tabulated in Table 3 highlighted the variability in EPC₀ with highest values recorded at surface bankside locations and a trend toward increasing values from A to G along the length of the ditch.

The boxplots in Fig. 4 illustrate increases in EPC₀ from A to G, coinciding with M3P recorded at downstream points compared to upstream sample points. Highest EPC₀ and M3P values downstream at G, indicate accumulation and deposition of P, that is loosely bound P (low *k* values) and released to water (EPC₀) therefore acting as a source of P to the overlying water and water draining into the ditch.

At all bankside depths at G, *k* values were low (<1 mg L⁻¹) and EPC₀ values ranged from 0.24 to 4.61 mg L⁻¹. The P dynamics at this point on the ditch indicate that deposition of P from upstream sources and water draining the site has altered the sediment P sorption characteristics towards net release of P to water. This is largely driven by accumulated P in bankside and sediment, that is loosely bound (low *k* values), making this junction at source of P leaving the ditch.

The relationship between *k* and EPC₀ in bankside and sediment samples is illustrated in Fig. 5 (a), showing the influence of binding energies on potential P release. Bankside and sediment *k* values accounted for 40% of the variation in EPC₀ values. Moloney et al. (2020) found a similar regression coefficient between *k* and EPC₀ measured in ditch sediment across 10 farms and also reported the influence of accumulated labile P in ditch sediment on EPC₀ values. A similar relationship between M3P and EPC₀ was observed and is plotted in Fig. 5 (b) demonstrating the positive relationship between accumulated labile P (M3P) and EPC₀ values, therefore supporting our suggestion that P deposition in ditches can act as a source of P to overlying water, thereby increasing the sediment EPC₀.

3.4. Impacts on water quality and source-sink properties of ditch sediments

The water quality and bankside-sediment data are both indicative of diffuse and point sources of P coming into the ditch network. A step change in water quality was observed at D, due to point source inputs from the yard, but the effect on sediment P dynamics and deposition occurred further downstream at E. These data signal the influence of the farm yard on water quality and sediment P deposition in agricultural ditches. Inputs from the yard acted as a direct point source of P into the ditch and a source of P accumulation in sediment, causing deterioration in water quality and altered P sorption dynamics of the bankside and sediment. Changes in sediment P were characterised by higher extractable P (M3P) and lower P binding energies. Furthermore, P inputs into the ditch altered the EPC₀ reducing the attenuation capacity of bankside

Table 3

Phosphorus (P) sorption isotherm parameters describing sorption maxima S_{max} , P binding energies k , and Langmuir model R^2 measured in bankside and sediment samples. Equilibrium P concentrations EPC_0 is derived from isotherms at low initial P concentrations. Accumulation of P is expressed as labile P using Mehlich extractable P from bankside samples at 30 cm depth intervals to the base and sediment samples taken from sample point A to G along the length of the ditch.

Location	Depth	Sorption properties			Equilibrium Phosphorus		M3P
Code	(cm)	S_{max} (mg kg ⁻¹)	k (L mg ⁻¹)	R^2	EPC_0 (mg L ⁻¹)	R^2	(mg kg ⁻¹)
Site A							
A1	0–30	208.33	0.85	0.98	0.40	0.99	32.81
Sediment	Base	200.0	0.728	0.98	0.06	1.00	42.98
Site B							
B1	0–30	285.71	1.093	0.95	0.07	1.00	14.22
B2	30–60	333.33	1.87	0.97	0.03	1.00	13.05
B3	60–100	322.58	1.55	0.98	0.14	1.00	31.49
Sediment	Base	196.07	0.850	0.98	0.44	0.99	19.72
Site C							
C1	0–30	357.14	0.58	0.95	1.71	0.92	83.98
C2	30–60	294.11	1.03	0.99	0.62	1.00	40.57
C3	60–90	357.14	2.33	0.97	0.06	1.00	26.97
*C4	90–110	n/a	n/a	0.42	0.01	1.00	9.1
Sediment	Base	131.57	0.5278	0.96	0.28	1.00	20.33
Site D							
D1	0–30	250.0	0.85	0.97	0.07	1.00	13.81
D2	30–60	370.62	1.57	0.977	0.05	0.99	11.42
D3	60–90	116.27	0.741	0.98	0.04	0.99	7.87
D4	90–110	81.96	2.440	0.91	0.04	0.99	15.7
Sediment	Base	163.93	2.902	0.97	0.25	1.00	28.09
Site E							
E1	0–30	285.71	0.66	0.98	2.05	0.99	97.36
E2	30–60	285.7	0.56	0.95	1.75	1.00	86.39
E3	60–90	256.41	0.81	0.96	0.75	1.00	59.73
E4	90–120	294.11	0.79	0.97	0.84	1.00	68.65
E5	120–150	243.90	0.69	0.96	0.35	1.00	38.25
E6	150–180	187.68	0.75	0.97	0.14	1.00	26.4
E7	180–210	400.0	2.50	0.9	0.00	1.00	5.4
E8	210–240	303.03	1.73	0.97	0.01	1.00	7.15
Sediment	Base	192.30	0.55	0.95	0.36	0.98	31.79
Site F							
F1	0–30	256.41	1.0	0.97	0.21	1.00	25.81
F2	30–60	217.39	0.75	0.96	0.12	1.00	14.23
F3	60–90	222.22	1.32	0.98	0.15	1.00	19.02
F4	90–120	185.18	0.675	0.96	0.18	1.00	17.37
F5	120–150	188.67	0.73	0.97	0.27	0.99	20.71
F6	150–180	151.51	0.55	0.97	0.35	0.99	20.08
F7	180–210	250.0	0.68	0.97	1.62	0.99	60.73
F8	210–240	250.0	0.68	0.97	1.11	0.99	59.18
F9	240–270	344.82	1.38	0.99	0.58	1.00	53.27
F10	270–290	333.33	1.50	0.98	0.42	1.00	28.77
Sediment	Base	285.71	0.89	0.96	0.41	1.00	50.1
Site G							
G1	0–30	285.71	0.49	0.99	4.61	0.94	101.49
G2	30–60	357.14	0.38	0.98	4.17	0.94	108.84
G3	60–90	416.66	0.48	0.97	2.98	0.89	111.36
G4	90–120	344.82	0.93	0.98	0.78	1.00	89.79
G5	120–150	285.71	0.74	0.98	1.19	0.88	86.78
G6	150–180	303.033	0.67	0.97	1.21	0.99	72.77
G7	180–210	256.41	0.92	0.98	1.00	0.99	80.19
G8	210–240	250.0	0.95	0.98	0.65	0.99	70.75
G9	240–270	178.57	0.708	0.97	0.46	0.99	40.88
Sediment		227.27	0.88	0.98	0.24	1.00	38

and sediments in the ditch. This is also evidenced by the positive correlation between M3P and EPC_0 highlighting the influence of P inputs on sediment ability to attenuate P.

The accumulated P in surface layers of E, coupled with lower k values, and consistently high DRP and TP concentrations show release of P from bankside sediment. This is similar to some deeper intervals of F and all intervals of G which were saturated with P and k values get lowers as P deposited into system. This caused a release of accumulated P into the water and thus higher DRP concentrations. This observation is also supported by EPC_0 values which are presented in Fig. 6 with mean bankside and sediment EPC_0 at each sampling point along the ditch, plotted against mean DRP values at each point. The plot include the (1:1) line of equality between EPC_0 and DRP values where points below the line indicate sediment acting as a P source and points above line

indicate a P sink (Smith et al., 2005). In Fig. 6 most of the EPC_0 values along this ditch, with the exception of values recorded at A and B, acted as source of P, releasing P to water.

The results highlighted the need for a mitigation intervention (McDowell and Nash, 2012) to clean ditch water before it leaves the farm (King et al., 2015).

This study identified the appropriate location for installation of an in-ditch nutrient interceptor at point D-E when the nutrient pollution starts to elevate before accumulating at point G. In-ditch engineered structures filled with medium/media with nutrient adsorption/remediation capacity can retain P before leaving the ditch and entering a surface water body (Ezzati et al., 2019). However, mitigation options should consider the high legacy P in deeper soil layers of the bankside and sediment samples which will continue releasing P into the water,

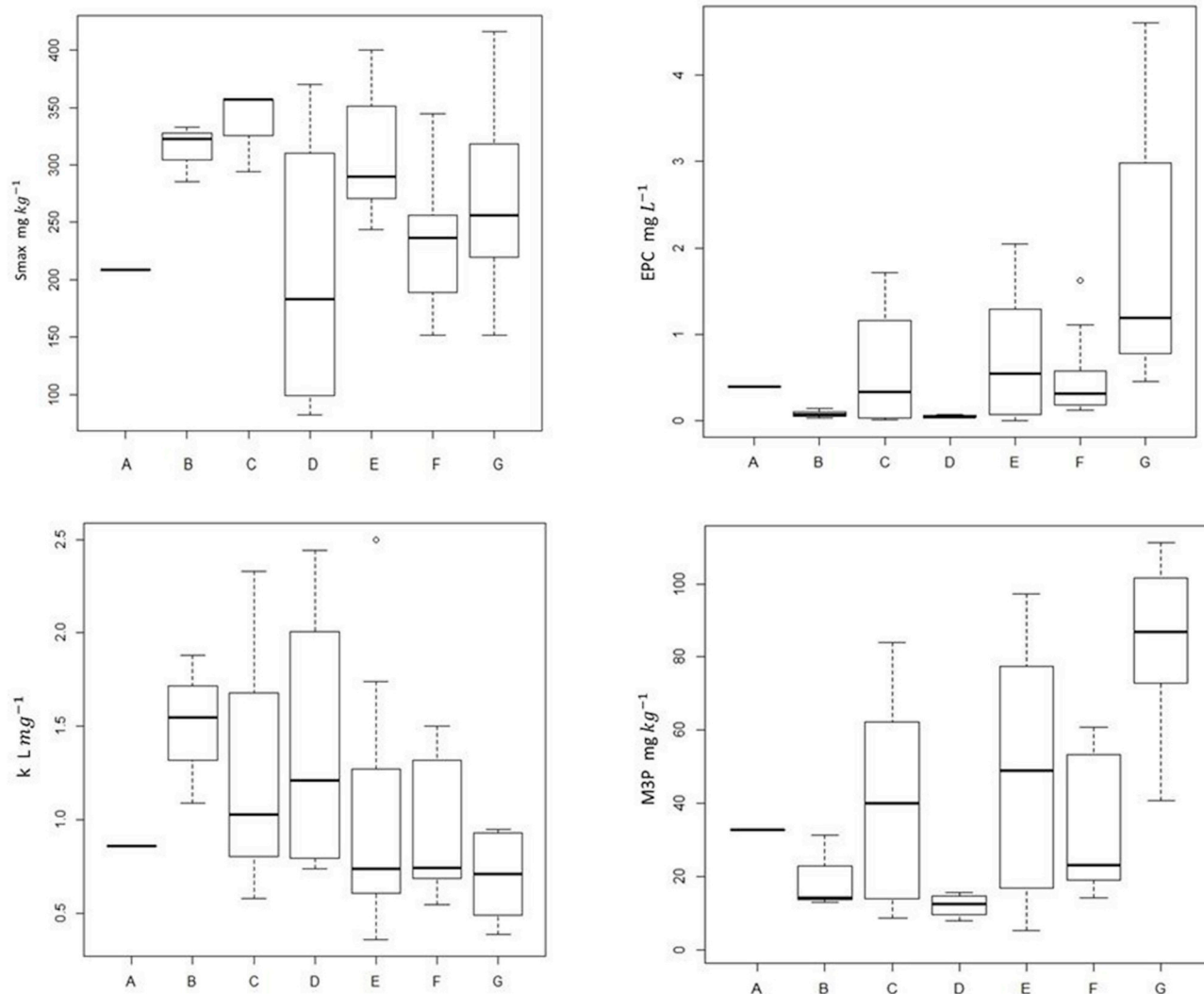


Fig. 4. Boxplots showing the distribution of Smax, EPC₀, k, and M3P values in all bankside and sediments at sampling locations A-G. The midline represents the median.

and which will delay and short term impacts on water quality.

4. Conclusion and recommendations

This study examined hydrochemistry and sediment P trends along the length and depth of an agricultural ditch network on an intensive dairy farm. High spatial resolution grab samples of ditch water were collected over 18 months alongside measurements of bankside and sediment P chemistry at depth intervals at points along the ditch. Phosphorus concentrations in water increased along the length of the ditch, due to inputs from a point source, identified by the presence of pipes discharging from the farm yard directly into the ditch. This caused a step-change in water P concentrations at this point as mean DRP and TRP values increased >10-fold from upstream to downstream points, indicating little or no attenuation of reactive P in the ditch by sediment. Particulate P increased sharply at the sample point closest to point source inputs from the yard, but values fell back in line with upstream values, indicating some attenuation of PP along the length of the ditch. Inputs from point and diffuse sources were transferred downstream resulting in deposition of P in sediment, which inhibited any natural attenuation of soluble P along the length of the ditch. The highest accumulation of P in the ditch sediment was recorded at the furthest downstream sampling point and P inputs into the ditch not only affected

water quality but altered the sorptive properties of the sediment toward acting as a secondary source of P to water leaving the ditch network. The effects of P inputs from the yard on water quality and sediment P characteristics did not coincide at the same point on the ditch, rather, the step change in water quality occurred at D whilst changes in sediment P were only evident further downstream at D, indicating transfer and deposition in ditch sediment. The results demonstrated that such P inputs have altered the physico-chemical characteristics of the ditch sediment which highlights the need to remediate sediment to restore its natural P attenuation capacity and reverse its role as a secondary source of P to water. Water quality policy design will need to account for physico-chemical the lag phases in sediment remediation before any improvements are observed. Preventing further point source inputs to the ditch requires substantial restructuring in the farm yard, such as, redirecting yard runoff entering ditches, directly or indirectly, by e.g. blocking the pipes and collecting runoff for water treatment.

Close circle: Average EPC₀ from bankside (mg L⁻¹), Open circle: EPC₀ (mg L⁻¹) values from sediment. Values below 1:1 line indicate that the point act as a potential source of P.

Author contribution section

All authors provided interpretation and analysis of data, written text

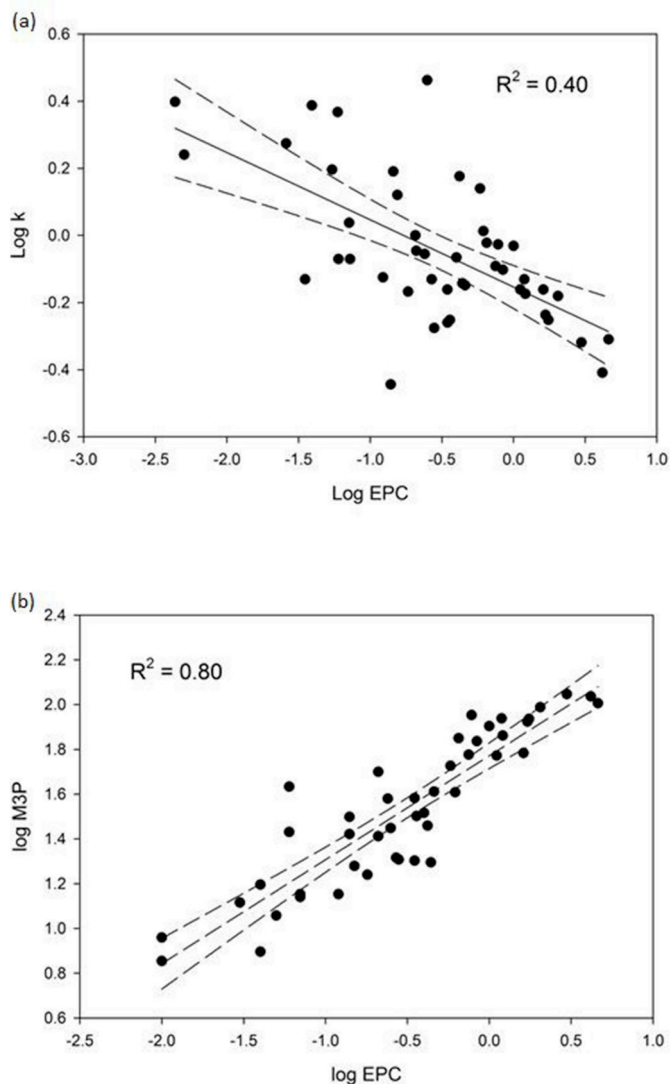


Fig. 5. Scatter plot showing (a) regression line between $\log EPC_0$ and $\log K$, and (b) regression line between $\log EPC_0$ and $\log M3P$ in all bankside and sediment samples.

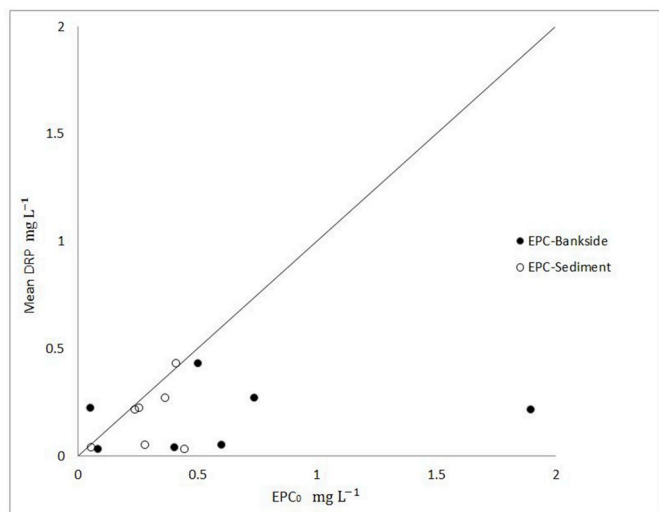


Fig. 6. Mean DRP values collected at sampling points as a function of average EPC_0 at bankside and EPC_0 of sediment.

and review of drafts of the manuscript. All authors contributed analytical data from field samples and laboratory assays to the database.

Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675120.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2019.109988>.

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