INTRODUCTION

Human-induced climate change is changing rainfall and the hydrological cycle (Trenberth, 2011). The first rainfall–runoff event following slurry application has the most impact in terms of exporting phosphorus (P) in runoff and so potentially degrades surface waters (Schroeder et al., 2004; Sharples, 1997; Watson et al.,...
2007). Climate-smart P management measures are needed to better prepare for the changes in the timing, intensity and duration of rainfall associated with climate change (Schoumans et al., 2015). To comply with the Nitrates and Water Framework Directives in Ireland, livestock slurries must not be applied to land if heavy rain is forecast within 48 h (European Commission, 1991, 2000).

Northern Ireland has poorly drained soils that are prone to runoff, while the total land application of livestock slurries and manures exceeds P requirements by 20%, indicating that targeting manure applications to avoid subsequent P losses via runoff should be an important consideration in manure management (Doody et al., 2010; Rothwell et al., 2020). This oversupply of P is most acute for dairy farms where over 50% of grasslands have soil test P values in excess of the agronomic optimum for grass production, index 2 (>25 mg Olsen P L soil⁻¹) (Higgins et al., 2020). In extensively managed grassland farms, 25% of fields had soil test P above the agricultural optimum. This suggests further implications of wet weather and wet soil for P management.

Using field and plot data for slurry applications and the rainstorm events on P loss, a model designed to simulate the dynamics of slurry P and surface runoff (SurPhos) showed that storm hydrology was the largest driver of slurry P loss to runoff irrespective of when the first rainstorm runoff event occurred (Vadas et al., 2017). This implies that soil adsorption of slurry P is not the main mechanism by which runoff P concentrations are reduced over time.

The objective of the current study was to examine the effect of increasing the time interval between dairy slurry application and the first rainstorm event on runoff P in a grassland sward, on the P signal in runoff. The experimental data were combined with the surface phosphorus and runoff model SurPhos to determine whether P in runoff could be predicted to better understand the processes controlling P loss.

2 | METHODS AND MATERIALS

2.1 | Experimental design

The experimental site was a permanent grassland field at Hillsborough, Northern Ireland (Irish grid reference: J244577), with slope of 3.5° and a slightly gleyed sandy clay loam overlying Silurian shale (O’Rourke et al., 2010). The site had a well-established silage sward, dominated by meadow grasses ( Poa trivialis and P. annua) and perennial ryegrass ( Lolium perenne). The soil organic matter content was 12%, the mean bulk density was 1.02 g cm⁻³, and the soil field capacity was 42.1% ( Cruickshank, 1997).

Two treatments were included in this study, dairy slurry with a total P content of 1.3% and a control treatment with no slurry. The slurry was produced on a dietary P input of 5.4 g P kg⁻¹ DM fed as a 50:50 ratio of concentrate (7.4 g kg⁻¹ DM) and grass silage (3.3 g P kg⁻¹ DM) fed to non-lactating Holstein dairy cows (O’Rourke et al., 2010). It was frozen at −20°C until required.

The field experiment was undertaken in late summer from 30 July to 18 September 2007 and was set up as a randomized block design with four blocks and six split plots (twelve runoff plots) in each block. Each block was a replication. Split plots allowed for slurry and control treatments to be paired together, whereby slurry and control plots were laid out side by side, to account for the effect of spatial variability within the site. Six time periods were randomly allocated to the split plots within each block. Plots were established following the National Phosphorus Research Project protocol (NPRP, 2001). Plots were 0.5 m² and hydrologically isolated to a depth of ca. 0.1 m in the soil by aluminium metal borders, and an aluminium runoff collector on the down slope (6% slope) transferred surface runoff to a 2-L collection vessel.

Slurry was defrosted and diluted to 6% DM with deionized water and applied by pouring at a rate of 50 m³ ha⁻¹, or 2.5 L of slurry per plot, which is the maximum allowable volumetric rate for slurry allowed under the code of good agricultural practice (Good Agricultural Practice for Protection of Waters (European Union), 2017; The Nutrient Action Programme Regulations (Northern Ireland), 2019). Slurry total P application rate was 40 kg P ha⁻¹.

Simulated rainfall was applied to plots at 2, 4, 10, 18, 30 or 49 days after slurry application. A portable drip-type rainfall simulator (Amsterdam Simulator; Bowyer-Bower & Burt, 1989) delivered rainfall at an intensity of 40 mm h⁻¹ for 30 min to simulate a storm event. Tap water was deionized in the field (DC9 general deionizing cylinder; Purite Limited) to overcome P concentrations in tap water (>0.8 mg P L⁻¹). Plastic cling film wrapped around the stand of the rainfall simulator served as a wind screen in the field.

Natural runoff that occurred between simulated runoff events was collected at approximately weekly intervals from each plot. Natural rainfall was recorded ca. 100 m from the site with a thirty-minute frequency by a tipping bucket rain gauge on a Delta-T Weather Station, calibrated to tip once for each 2 mm of rain and recorded by a Delta-T logger. Air temperature was recorded daily at 30-min intervals. Soil moisture was measured in each plot prior to rainfall simulations using a Theta Probe ML1 soil moisture sensor (AT Delta Devices).

Dissolved reactive P (DRP) in runoff was determined on 0.45-μm filtered (Millipore) samples and analysed by
the acidic molybdate–ascorbic acid method of Murphy and Riley (1962). Total P and total dissolved P in runoff were determined on filtered and unfiltered samples, digested with potassium persulphate and sulphuric acid (Eisenreich et al., 1975), and analysis of the digest was performed as per Murphy and Riley (1962). Particulate P (PP) was calculated as the difference between TP and TDP, and dissolved unreactive P (DUP) was calculated as the difference between TDP and DRP. Slurry total P was determined on ashed samples, and water-soluble P was extracted from fresh slurry on a dry weight equivalent basis with deionized water at a 100:1 ratio by a modification of the Self-Davis and Moore (2000) method (Kleinman et al., 2007), both slurry fractions were then analysed as per Murphy and Riley (1962). Soil samples (0–75 mm) were determined on filtered and unfiltered samples, dissolved unreactive P in Figure 1. The P concentrations were highest when

\[ \text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{n}} \]  

where \( \Sigma \) is the sum, \( \hat{y}_i \) are the predicted values, \( y_i \) are the observed values, and \( n \) is the sample size.

### 3. RESULTS

#### 3.1 The effect of increasing the time interval between slurry application and the first rainstorm event on P concentrations in runoff

Increasing the time between slurry application and the first simulated rainstorm event resulted in decreasing P concentrations in runoff. This is shown for dissolved reactive P in Figure 1. The P concentrations were highest when
a rainstorm event occurred on day 2 and reduced steadily thereafter with an increase in the number of days between slurry application and the first simulated rainstorm. An elevated P signal in runoff from slurry persisted until at least day 18, and by day 30, the P concentrations were similar to the control. After day 30, soil and/or slurry mineralization may have caused the small spike in P concentrations measured on day 49. The pattern of rainfall over the experiment was such that soil moisture had approached field capacity prior to the day 18 rainstorm event (field capacity is 42.1%), but subsequently, the soil was drying out with decreasing soil moisture on days 30 and 49.

The overall pattern in P concentrations is reflected by the statistical analysis. The total P concentrations in runoff from the slurry were found to be significantly different from the control up to day 18 and again on day 49 (Table 1). On day 10, the total P statistic means departed from the arithmetic means and this was because of variation in the control treatment. The control total P concentrations ranged from 0.6 to 2.2 mg P L⁻¹, and runoff was not generated for some plots. Within the constraints of the model (missing values and large variance at day 10), the statistics on day 10 do not show a difference between slurry and control total P concentrations. Nonetheless, the overall pattern of decreasing P agrees with observations. This applies to total and dissolved reactive P fractions.

Results of the REML (Table 2) showed that there was a significant difference between the slurry and control treatments for total P and dissolved reactive P fractions. There was no effect of time on P concentrations when the interval between the application of slurry and the first rainfall runoff event was varied, and as a result, there was no significant time slurry interaction. This is thought to be because of a large variation in the control masking the time effect.

In comparison with particulate P and dissolved unreactive P, DRP was the largest P fraction of TP in all runoff events, including runoff from the control plots (Figure 2). For example, TP in runoff from the slurry plots 2 days after application consisted of 81% DRP, 15% PP and 4% DUP. As a result, the time series of TP reflected changes in DRP (Figure 1). Increasing the interval between slurry application and the first simulated rainstorm event resulted in a non-linear decrease of P in runoff. DRP concentrations were highest during the first rainstorm event on day 2 and reduced steadily thereafter with subsequent first rainstorms following slurry application.

### 3.2 Influence of natural rainfall prior to simulated runoff events

Natural runoff was collected weekly and analysed to study the effect of any preceding rainfall on the P concentrations from simulated rainstorm events. Phosphorus concentrations in natural runoff were within the range and followed the pattern of P concentrations from simulated events. For example, following slurry application the dissolved reactive P concentrations (Figure 3) on day 2 declined up to day 18 (the previously defined P signal) and these P concentrations continued to decline to day 25 in natural runoff. A small spike in P concentrations was detected at day 29 and day 42 in natural rainfall before the final simulated event at day 49. The cumulative pattern of dissolved reactive P concentrations in runoff shows a natural logarithm over time (Figure 4). This was investigated further by running the data with the SurPhos model.

### 3.3 Predictions of runoff P by SurPhos

There are three inputs to the SurPhos model, average daily rainfall, average daily temperature and runoff volume.

| P fraction | Slurry treatment | Runoff day (days after slurry application) |
|------------|------------------|---------------------------------------------|
|            |                  | 2  | 4  | 10 | 18 | 30 | 49 | mg L⁻¹ |
| TP         | 1.3% P slurry    | 5.9| 3.9| 2.6| 2.1| 1.2| 1.3|
| Control    |                  | 1.1| 1.7| 0.1| 0.5| 1.2| 0.7|
| SEMa       |                  | 0.2| 0.1| 0.1| 0.1|    |
| Σ²b        |                  | <0.01| <0.01| NS| <0.01| NS| <0.05|
| DRP        | 1.3% P slurry    | 4.8| 2.5| 2.1| 1.5| 0.7| 0.9|
| Control    |                  | 0.9| 0.9| 0.1| 0.3| 0.6| 0.6|
| SEMa       |                  | 0.2| 0.2| 0.1|    |    |
| Σ²         |                  | <0.05| <0.05| NS| <0.01| NS| NS|

*Standard error of the mean.

*Chi-square distribution.

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**TABLE 1** Effect of increasing the number of days between slurry application and the first rainstorm event on concentrations of phosphorus fractions in runoff.
Daily rainfall totals and air temperatures for the experimental period are shown in Figure 5. Total rainfall that occurred over the 49 days of the experiment was 150.6 mm with intense rainfall on days 6 (27 mm) and 12 (44 mm). As the experiment occurred over a relatively short period in late summer, daily air temperatures were narrowly constrained with a median of 14.5°C. Soil moisture demonstrates a soil-drying effect after day 20, with observations shown in Figure 5 on days 2, 4, 10, 18, 30 and 49, and representing the average soil moisture across all plots receiving simulated rainfall on those days. Runoff volume was variable between treatments, with runoff volume from the control often greater than the slurry treatment.

No general relationship was found between runoff-to-rain ratios and dissolved reactive P concentrations. For example, low runoff-to-rain ratios resulted in both low and high P concentrations. Despite this, SurPhos was able to predict dissolved reactive P to a satisfactory level of accuracy.

Figure 6a shows SurPhos predicted dissolved reactive P concentrations in runoff in simulated rainstorm events for the slurry treatment plotted against the chemical measurements. Figure 6b shows the same SurPhos predictions with preceding natural runoff events included as inputs to the model. The correlation coefficient does not differ greatly ($R^2 = .89$ and .85, RMSE = .56 and .64) as a result of adding natural runoff data. Results of a two-sample t test (Table 3) indicate there is no significant difference between SurPhos predicted dissolved reactive P concentrations from simulated rainstorm events with or without natural runoff.

### 3.4 | SurPhos model

The SurPhos model output can be used to understand the dynamics controlling slurry P characteristics and dissolved P concentrations in runoff. Figure 7 shows the combined impact of the decomposition, mineralization and bioturbation processes in the model on slurry P fractions over the 50-day experiment. The plot shows the slurry inorganic and organic water-extractable P and the inorganic and organic non-water-extractable P, as well as slurry mass. Note that this plot is an output from a 49-day simulation for a slurry plot. The impact of the simulated rainstorm event on either manure mass of the P fractions in manure is minimal by day 49. Mineralization of inorganic water-extractable phosphorus is observed after day 25 (Figure 7), as noted in Figure 3 in dissolved reactive phosphorus concentrations. This is evidence for the elevated P concentrations in runoff following the defined P signal.

Slurry P mineralization rate is highest for the 49-day simulation (Figure 8). Earlier rainstorm events on days 2, 4, 10, 18 and 30 removed P from the plots with less slurry P available to be mineralized over time.

| P fraction | Fixed term  | Wald statistic | d.f. | Wald statistic/d.f. | Σ2c |
|------------|-------------|----------------|------|---------------------|------|
| TP         | Timea       | 7.5            | 5    | 1.5                 | NS   |
|            | Slurryb     | 8.3            | 1    | 8.3                 | <0.01|
|            | Time x slurry | 5.8           | 5    | 1.2                 | NS   |
| DRP        | Time        | 8.4            | 5    | 1.7                 | NS   |
|            | Slurry      | 10.0           | 1    | 10.0                | <0.01|
|            | Time x slurry | 6.0           | 5    | 1.3                 | NS   |

*aNumber of days after slurry application (2, 4, 10, 18, 30 or 49 days).

*bSlurry treatment (slurry, control).

4 | DISCUSSION

In the current study, the length of the P signal in runoff was determined in accordance with the USEPA threshold of 1 mg P L$^{-1}$ maximum desirable dissolved reactive P concentration in agricultural runoff (USEPA, 1986), in addition to the period of time when there was a statistical difference with the control treatment. This confirmed a P signal of up to 18 days in runoff following slurry application to grassland. Although some P did continue to be mobilized in runoff up to day 49, the difference between the slurry treatment and the control in dissolved reactive P was <1 mg P L$^{-1}$.

Increasing the time interval between slurry application and the first rainstorm event has been shown to reduce P loss in runoff, in both grassland and arable systems in other countries (see Vadas et al., 2011). The literature in this area provides the evidence base for the guidelines issued to land managers of ‘no slurry spreading if heavy rain is forecast within 48 h’. Some of the shortest P signals were
**Figure 2** Total phosphorus (TP), dissolved reactive phosphorus (DRP), particulate phosphorus (PP) and dissolved unreactive phosphorus (DUP) concentrations in runoff vs timing of first simulated rainfall for (a) slurry and (b) control treatments.

\[
\begin{align*}
  y &= -1.5\ln(x) + 6.5 \quad R^2 = 0.8 \\
  y &= -1.2\ln(x) + 5.0 \quad R^2 = 0.8 \\
  y &= -0.2\ln(x) + 1.0 \quad R^2 = 0.6 \\
  y &= -0.1\ln(x) + 0.4 \quad R^2 = 0.5
\end{align*}
\]

**Figure 3** Dissolved reactive phosphorus concentrations in runoff from simulated storm events and natural runoff. N; total natural runoff generated for ~1-week period. Natural runoff represents the runoff that preceded simulated rainstorm events only. No natural runoff was generated between day 42 and day 48 (48N).
reported, that is 3 and 3.5 days, when liquid poultry slurry or dairy slurry was applied to grassland followed by immediate rainfall (Preedy et al., 2001; Westerman & Overcash, 1980). In these cases, the runoff P concentrations diminished quickly with a high rate of slurry P removal from the plots. At the other extreme, elevated P concentrations in runoff were observed for one hundred and eight days after fertilizer (50 kg N, 45 kg P and 125 kg K ha⁻¹) was incorporated to a depth of 15 cm before planting maize (Gascho et al., 1998). In this experiment, P concentrations of an initial 7 mg P L⁻¹ declined to 1 mg P L⁻¹ over consecutive rainfall events at 1, 4, 29, 49 and 108 days. A longer P signal of 19 months was reported after broiler litter was broadcast to grassland plots (Pierson et al., 2001). The rainfall inputs were natural in this experiment (rainfall averaged 1299 mm year⁻¹), and the initial runoff P was high (18 mg P L⁻¹) but the dissolved reactive P concentrations were strongly related to the natural algorithm of days after application and runoff volume. It is worth noting that the study by Pierson et al. reflected normal grassland management and the plots were stocked, either with continuous or with rotational stocking, and there was no effect of stocking management on runoff water quality. Within these two extremes of very short and very long P signals in runoff, the majority of studies reported elevated P concentrations for around 2–4 weeks (examples are Edwards et al., 1994; Kleinman & Sharpley, 2003; Schroeder et al., 2004; Sharpley, 1997).

In Ireland, there is a lack of studies on the effect of rainfall timing on runoff P loss. A study investigating the seasonal effect of runoff P following dairy slurry with varied slurry P content reported elevated concentrations of runoff P for 28 days in spring and 9 days in summer and winter (O’Rourke et al., 2010). This study was conducted with repeated rainfall simulations at 2, 9, 28 and 49 days. Low-emission slurry spreading by trailing shoe was compared to splash plate application over repeated simulated events at 2, 9 and 28 days ( McConnell et al., 2016).
The splash plate method resulted in higher initial P concentrations on day 2 (>1.5 fold the DRP concentrations from trailing shoe). Yet, at day 28 higher P concentrations in runoff in the trailing shoe treatment indicated more slurry on the soil surface was contributing to a longer P signal.

The results of the current study demonstrate that when immediate rainfall is avoided for up to two days, slurry remains on the plot and there is a reduction in the risk of runoff P loss over time (Figures 1 and 8). The current guidelines on when to apply slurry do not convey this risk and are therefore not adequately communicating to farmers that P may continue to be lost from fields to watercourses beyond two days. Furthermore, research on runoff initiation from a drumlin grassland hillslope in Ireland showed that 59% of runoff events occurred on days when soil moisture was below field capacity. Rainfall intensity was the most important variable in determining the probability of runoff (Doody et al., 2010). Better agronomic advice that considers the effect of management and slurry P interaction with runoff is needed in the context of the Irish climate for better environmental outcomes.

The results of the current study showed a reduction in runoff P concentrations over time with a P signal lasting for an 18-day period. The subsequent spike in P concentrations was unexpected. Particularly, as DRP concentrations in natural runoff collected at days 29 and 42 were higher than the simulated event at the end of the experiment with a rainstorm at day 49. This spike in P concentrations was assumed to be soil/slurry P mineralization, but this was not measured in the current study.

To understand the effect of rainfall and runoff characteristics in this study on slurry–runoff interaction, the SurPhos model was employed. This model has been well validated against a number of studies using a variety of slurry types, that is swine, poultry and dairy slurry (Vadas et al., 2011). SurPhos simulates decomposition, mineralization and bioturbation processes and has shown, regardless of the number of days to the first rainstorm event, it is rainstorm hydrology that will significantly affect slurry P loss because of an interdependence of slurry P, rain and runoff. In the current study, the rainstorm hydrology observed did not reflect the pronounced relationship shown between runoff-to-rain ratios and dissolved reactive P concentrations in 9 other studies (Vadas et al., 2011). Nevertheless, the model outcomes found the simulated runoff events to be predicted to a similar level of accuracy (Figure 6a, $R^2 = .89$, RMSE = .56) because of the slurry P availability predicted as a function of rainfall and temperature. When preceding natural runoff, collected on a weekly basis, was included in the model, the accuracy did not change much (Figure 6b, $R^2 = .86$, RMSE = .64) under a scenario of P removal from the slurry to runoff prior to the timed simulated events. Overall, P concentrations in natural runoff were low compared with the simulated storm events (Figure 3) early in the experiment despite more rainfall (Figure 5).

The slurry P components predicted by the SurPhos model showed mineralization of slurry P beginning around day 26, which explained the peak in P concentrations after the defined P signal of 18 days (Figure 7). Slurry P mineralization was in fact observed to be occurring at low levels at intervals following heavy rainfall throughout the experiment (see the 49-day simulation in Figure 8), but in the later part of the experiment, as the soil begins to dry, a greater rate of mineralization occurred that gave rise to elevated P concentrations in runoff.
The current study shows the value of modelling experimental data to characterize the processes controlling the release of slurry P to runoff. These data could be extrapolated to study different weather scenarios to define the length of the runoff P risk period following slurry P applications in Ireland. Combined with a recent regional soil P survey (Higgins et al., 2020) showing where high soil test P is concentrated, around high grazing and accessible land, such an assessment could aid in creating solutions on where and when to safely spread slurries, in order to reduce P loss from farms, particularly in the context of climate-smart P management.

5 | CONCLUSION

This study investigated the impact of increasing the number of days between the application of dairy slurry and the first rainstorm-runoff event on runoff P concentrations from grassland. Increasing the number of days from 2 to 49 days after slurry application resulted in a decrease in P concentrations in runoff (5.01 to 0.97 mg DRP L⁻¹) and a P signal in runoff that lasted for 18 days. The SurPhos model was successfully used to predict dissolved reactive P concentrations in runoff despite variable runoff-to-rainfall characteristics. Adding preceding natural runoff as an input to the SurPhos model did not adversely affect the models’ ability to predict runoff P concentrations. The modelled slurry P dynamics were used to understand the risk period for elevated P concentrations in runoff. Utilizing these experimental data in SurPhos modelling has the potential to be used to test risk periods particularly in high soil test P soils, under scenarios of changing climate.

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DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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