

Dynamics of Measured and Simulated Dissolved Phosphorus in Runoff from Winter-Applied Dairy Manure

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Abstract

Agricultural P loss from fields is an issue due to water quality degradation. Better information is needed on the P loss in runoff from dairy manure applied in winter and the ability to reliably simulate P loss by computer models. We monitored P in runoff during two winters from chisel-tilled and no-till field plots that had liquid dairy manure applied in December or January. Runoff total P was dominated by nondissolved forms when soils were bare and unfrozen. Runoff from snow-covered, frozen soils had much less sediment and sediment-related P, and much more dissolved P. Transport of manure solids was greatest when manure was applied on top of snow and runoff shortly after application was caused by snowmelt. Dissolved P concentrations in runoff were greater when manure was applied on top of snow because manure liquid remained in the snowpack and allowed more P to be available for loss. Dissolved runoff P also increased as the amount of rain or snowmelt that became runoff (runoff ratio) increased. The SurPhos manure P runoff model reliably simulated these processes to provide realistic predictions of dissolved P in runoff from surface manure. Overall, for liquid dairy manure applied in winter, dissolved P concentrations in runoff can be decreased if manure is applied onto bare, unfrozen soil, or if runoff ratio can be reduced, perhaps through greater soil surface roughness from fall tillage. Both management approaches will allow more manure P to infiltrate into soil and less move in runoff. SurPhos is a tool that can reliably evaluate P loss for different management and policy scenarios for winter manure application.

Core Ideas

- Better information is needed on winter P loss in runoff from winter-applied manure.
- Winter runoff after manure application is dominated by dissolved P.
- Event hydrology exerts a strong control on runoff dissolved P concentrations after manure.
- The SurPhos model can reliably estimate dissolved P loss in runoff for winter manure application.

AGRICULTURAL nutrient management is a research and policy issue due in part to phosphorus (P) loss in runoff and subsequent water quality degradation (Parris, 2011; Sharpley, 2016). Manure applied to fields without incorporation is an important source of P loss (Good et al., 2012), especially dissolved P that has high bioavailability in aquatic systems (Baker et al., 2014). For surface-applied manure, maximum dissolved P loss occurs when manure with highly available P is applied during times of high runoff probability (Owens et al., 2011; Vadas et al., 2017). In the northern United States and Canada, winter and early spring are periods of frequent runoff from snowmelt and rain-on-snow events on frozen soils. In some states, winter dairy manure application is common because it reduces the need for manure storage, allows time for spreading when there are fewer field activities, and reduces soil compaction from equipment when soil is frozen (Lewis and Makarewicz, 2009; Liu et al., 2017). Because winter-applied manure is typically not incorporated, the combination of surface manure and high runoff potential has prompted states to restrict winter spreading (Srinivasan et al., 2006; Liu et al., 2018).

Processes controlling manure dissolved P runoff during winter vary widely depending on P cycling, weather, frozen soil conditions, and runoff hydrology, as well as manure spreading practices, especially placement on top of snow and the effect of manure on rates of snowmelt (Kongoli and Bland, 2002; Vadas et al., 2018; Stock et al., 2019b). Studies that investigate and report the biochemical and hydrologic processes that control dissolved P runoff transport after manure application are limited. Most studies have been observational at the plot to field scale with conflicting results regarding how much winter manure application increases P runoff relative to other seasons, often because of annually variable weather, frozen soil conditions, and runoff hydrology. Much research was conducted before 1980 (Converse et al., 1976; Klausner et al., 1976; Young and Mutchler, 1976; Young and Holt, 1977; Phillips et al., 1981; Steenhuis et al., 1981), with some more recently (Hansen et al., 2000; Ulén, 2003; Lewis and Makarewicz, 2009; Komiskey et al., 2011; Owens et al., 2011; Singh et al., 2017). Recent research

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Abbreviations: CT, chisel tillage; NSE, Nash–Sutcliffe model efficiency; NT, no-till; RSR, the ratio of root mean square error to the standard deviation of observed values; SWE, snow-water equivalent; WEP, water-extractable phosphorus.

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(Williams et al., 2011, 2012a, 2012b; Vadas et al., 2018) has investigated winter processes and manure P loss at the controlled laboratory scale, but there remains a definite lack of similarly focused data from field studies under natural conditions. This makes it difficult to develop scientifically based winter manure application recommendations that can consistently reduce P loss for a variety of conditions and practices.

The research reported here is part of a series of experiments designed to improve understanding and modeling of processes controlling runoff and nutrient loss from winter-applied manure (Vadas et al., 2017, 2018; Stock et al., 2019b). Our objectives were (i) to describe how manure application timing and runoff hydrology control dissolved P concentrations in runoff from field plots receiving liquid dairy manure, and (ii) to determine if the SurPhos manure P runoff simulation model (Vadas et al., 2007) can reliably predict dissolved P concentrations in runoff for the experimental winter conditions. Stock et al. (2019a) describe the approach used in the field study and the effects of application timing and tillage on nutrient runoff loads (kg ha^{-1}). This paper focuses on dissolved P runoff concentrations to better understand and model P runoff dynamics as a function of source (P available in manure) and hydrology (both the rain and snowmelt water that mobilizes available manure P and the percentage of this water that becomes runoff). Throughout, the term “runoff ratio” refers to the ratio of runoff water to the total water that interacted with manure, including rain, snowmelt, or both. Finally, Vadas et al. (2017) successfully used SurPhos to simulate winter manure P in runoff for data from two Wisconsin field studies. In one study, manure was never applied onto snow, and the second study was on a commercial farm where there was uncertainty about manure application rates and P contents. For the second study, the authors also had to make assumptions about liquid manure P availability when applied on top of snow to improve model predictions. Our current evaluation provided an opportunity to test SurPhos using more controlled field data.

Materials and Methods

Field Site Description and Measurements

The site was at the University of Wisconsin–Madison Arlington Agricultural Research Station (AARS; $43^{\circ}17' \text{ N}$, $89^{\circ}21' \text{ W}$). Study details are given by Stock et al. (2019a) and only briefly described here. There were 18 plots (each 5 m wide \times 15 m long) with two tillage and three manure timing treatments in a complete factorial design on a 5.8%, south-facing slope with silt-loam texture. During the study (2015–2017), plots were cropped in corn (*Zea mays* L.) for silage with field operations performed perpendicular to the downhill 15-m plot length. Tillage treatments were fall chisel tillage (CT) with a soil finisher pass in the spring and no-till (NT) and resulted in rough and smooth soil surfaces during the winter. Manure treatments were early December application, late January application, and an unmanured control. All treatment combinations had three replications. We applied liquid dairy manure (2–6% solids) at 37.4 kL ha^{-1} , which was a function of local regulations, and analyzed manure for total solids and total P (University of Wisconsin Soil and Forage Analysis Laboratory) (see Stock et al., 2019a, for data). Manure TP application rate ranged from 8.7 to 11.3 kg ha^{-1} the first winter, and 14.4 to 17.8 kg ha^{-1} the second winter.

For SurPhos modeling, we assumed manure water-extractable P (WEP) was 50% of total P (Kleinman et al., 2005).

An onsite weather station measured air temperature and precipitation as rain or liquid equivalent of snow. We measured ground snow depth and density on plots to estimate snow-water equivalent (SWE) at least weekly and up to daily during precipitation and thaw events. A collection system that used a series of buckets with water-dividing crown heads measured runoff from each plot (Bonilla et al., 2006; Vadas and Powell, 2013). We collected water samples at the end of each runoff event and stored them at 4°C until analysis. We measured runoff solids content gravimetrically after oven drying samples, analyzed unfiltered samples for total P colorimetrically after Kjeldahl digestion (AQ2 Discrete Analyzer, SEAL Analytical Brand), and filtered runoff samples ($0.45 \mu\text{m}$) for dissolved reactive P colorimetrically (Murphy and Riley, 1962). All runoff hydrology and P concentrations data presented in the paper for specific runoff events are means of the plot replications that actually produced runoff. For 39 events, 36 had runoff from all three replicates, and only three had runoff from two replicates.

SurPhos Manure P Runoff Modeling

SurPhos is a daily time-step model that simulates surface application of manure and dissolved P loss in runoff, as well as soil P cycling (Vadas et al., 2007). Because SurPhos was designed to be integrated into larger field or watershed models to improve how they simulate agricultural P cycling (Sedorovich et al., 2007; Collick et al., 2016; Liu et al., 2017), it does not simulate all processes that affect P loss in runoff namely crop growth, runoff, or soil erosion and particulate P loss. SurPhos requires input data for initial soil P content, amount of manure applied, moisture and P content of manure, daily average temperature, and daily precipitation and runoff. Experimental data from the field study provided all the necessary inputs.

SurPhos simulates both manure WEP and non-water-extractable P (Non-WEP). Only WEP is available for release during a rain or snowmelt event and loss in runoff. SurPhos also simulates inorganic soil P cycling and dissolved loss in runoff. Users specify the day and rate of manure application, manure P content, and application method. If liquid manure ($<15\%$ solids) is applied, SurPhos assumes 60% of manure P infiltrates into soil and is unavailable for direct loss in runoff. After application, the model simulates manure decomposition and assimilation into soil, and conversion of Non-WEP into WEP. When rain or snowmelt occurs, SurPhos simulates manure WEP release based on the ratio of water volume to manure mass ($\text{cm}^3 \text{ g}^{-1}$). Dissolved P in runoff is estimated by multiplying this released P by a unitless P distribution factor (P_d), which is a function of the runoff ratio. Overall, SurPhos considers both manure properties and storm hydrology when estimating P loss in runoff, but it is largely the event hydrology, as represented by the amount of rain or snowmelt and the runoff ratio, that control both P concentrations and loads in runoff.

In SurPhos for rain-only events, the amount of water that can release manure WEP is measured precipitation. For snowmelt events, mobilizing water is the difference in SWE before and after an event (Vadas et al., 2017). In this project, we used measured snowfall to estimate inputs of available snow water onto plots and estimated daily snowmelt using a degree-day method where the snowmelt rate was $2.5 \text{ mm } ^{\circ}\text{C}^{-1}$ (mean daily air temperature)

greater than 0.0 (USDA-NRCS, 2004). We estimated how much snowmelt, as well as any rain, was absorbed by snow before it became free-flowing water and interacted with manure. To do this, we assumed that the depth of fresh snow was 12 times the water equivalent depth and that snow could absorb water up to 6% of its depth. For example, if 100 mm of snow fell (actual snow depth), it could absorb 6 mm of water (either snowmelt or rain). If there were 3 mm of snowmelt (water equivalent) and 2 mm of rain, snow absorption capacity was reduced to <1 mm (less snow would reduce absorption capacity as well as an increase in absorbed water) and remained there until more snowmelt or rain occurred to decrease absorption capacity or new snow fell to increase capacity. We used a daily amount of liquid water present that exceeded snow absorption capacity to simulate interaction with manure. Throughout this process, we adjusted estimated SWE data so they matched measured SWE data. For example, if decreases in measured SWE occurred during days of freezing temperatures, we assumed decreases were due to sublimation or snow drift (and not snowmelt) and decreased estimated SWE to match measured values and not overestimate snowmelt later on. Throughout, we did not consider manure placement in the snowpack as a variable that needed to be accounted for in modeling snowmelt water interaction with manure (Vadas et al., 2018).

We compared measured and simulated dissolved P concentrations in runoff for the 2 yr of field data, using regression methods to evaluate model performance, including slope, intercepts, Nash–Sutcliffe model efficiency (NSE), RMSE, and the ratio of RMSE to the standard deviation of observed values (RSR) (Moriassi et al., 2007; Bennett et al., 2013; Bolster and Vadas, 2013). We evaluated if slopes relating measured and predicted values were different than 1.0, and if intercepts were different from 0.0 ($p = 0.05$). Nash–Sutcliffe efficiencies range from $-\infty$ to 1. An efficiency of 1 means a perfect match of modeled and observed data, 0 indicates model predictions are as accurate as the mean of observed data, and <0 is when the observed mean is a better predictor than the model. The RMSE is a measure of the average difference between predicted and observed values. The RSR varies from an optimal value of 0, which indicates zero RMSE and perfect model simulation, to a large positive value.

Results and Discussion

Field Runoff Hydrology

In 2015 to 2016 between early December and late March, there were a maximum of five runoff events after manure application from any treatment and a minimum of one (Table 1, Fig. 1). The CT plots generally had less runoff frequency and magnitude because rougher surface conditions created depressional storage that retained water (Table 1, Fig. 1) (see details in Stock et al., 2019a). The early December and late March runoff events were due to rain on bare, unfrozen soil. Events in between these times were due to rain-on-snow and snowmelt-only events. In 2016 to 2017 between early December and late March, there were a maximum of nine runoff events from any treatment after manure application and a minimum of four (Table 1, Fig. 2). The NT plots still had greater runoff frequency and magnitude, but not to the extent as in 2015 to 2016 (Table 1, Fig. 2). The majority of events were rain-on-snow events, with only the last event in late February being due to rain on bare soil (Table 1, Fig. 2).

Runoff Dissolved Phosphorus Dynamics

The 10 Dec. 2015 manure application was on unfrozen, bare soil. After application, there were five runoff events from NT plots and one from CT plots (Fig. 1, Table 1). The 26 Jan. 2016 manure application was on top of snow, with soil frozen to 50 cm. After this application, there were five runoff events from NT plots and one from CT plots (Fig. 1, Table 1). The 9 Dec. 2016 application was on top of snow overlying soil frozen to 10 cm, followed by nine runoff events from NT plots and four from CT plots (Fig. 2, Table 1). The 27 Jan. 2017 application was on top of snow overlying soil that was thawed at the surface but frozen from 6 to 44 cm. After application, there were four runoff events from NT plots and one from the CT plots (Fig. 2, Table 1). Snow depths at times of manure application ranged from 10 to 20 cm (Stock et al., 2019b).

The two winters represented a wide range of runoff conditions from bare (no snow), unfrozen soil to snow-covered, frozen soil. For bare soils, including no-manure controls, total runoff P across 21 events (considering manure treatments, tillage treatments, and controls separately) was dominated by nondissolved forms, with dissolved P accounting for only 9.5% (SD = 9.4%) of total P. In contrast, across 42 events from snow-covered, frozen soils, dissolved P accounted for 67% (SD = 21%) of total runoff P. This is in part a function of much less solids in runoff from frozen soil. Runoff solids from snow-covered, frozen soils ranged from 23 to 4456 mg L⁻¹ (median of 339 mg L⁻¹) and from bare soils ranged from 1311 to 12,270 mg L⁻¹ (median of 2176 mg L⁻¹). Given the importance of this dissolved P transport in winter runoff, the section below details its dynamics.

For the 2015 December manure application, the greatest dissolved P in runoff (0.95 mg L⁻¹, Fig. 3) was from NT plots in the first event after application, which occurred 3 d after application and was a rain event on bare, unfrozen soil (Fig. 1, Table 1). One reason for this relatively low runoff P concentration is because manure was applied to bare, unfrozen soil and had a chance to infiltrate into soil at application, leaving less manure P on the surface available to runoff. SurPhos assumes that such liquid infiltration decreases manure P on the surface by 60% (Vadas, 2006). A second reason is that this runoff event had a low runoff ratio (~1.6 mm of runoff vs. 49.6 mm of rain), meaning that most of the manure P mobilized by rain during the event infiltrated into soil rather than moving in runoff (Vadas et al., 2011). After this first event, runoff dissolved P from NT plots decreased to a steady concentration (average of 0.26 mg L⁻¹) that was similar to control plot concentrations (average of 0.16 mg L⁻¹). This decrease is due to declines in manure P content due to leaching of P out of manure over time by snowmelt and rain. The only runoff event from CT plots after the December application was on 20 February, and runoff dissolved P (0.13 mg L⁻¹) was similar to that from NT plots with the same manure application (0.26 mg L⁻¹) or control plots.

The 2016 January manure application had much greater (~4–5 mg L⁻¹) runoff dissolved P from NT plots in the first events after application than the earlier December 2015 application (Fig. 3). One reason is that the January application was on top of snow; thus, the manure liquid remained in the snowpack and increased the manure P available to runoff (Vadas et al., 2017, 2018). Another reason was that runoff ratios (Table 1) for events

Table 1. Date, hydrological conditions, and precipitation, snowmelt, and runoff for chisel-tilled (CT) and no-till (NT) plots during the 2015–2016 and 2016–2017 winter monitoring periods. Runoff ratios referred to in the text are calculated by dividing runoff amounts for a given event by the rain + snowmelt water amounts for the same event.

Date	Condition	Rain + snowmelt	Runoff			
			CT		NT	
			Dec.	Jan.	Dec.	Jan.
mm						
13 Dec. 2015	Rain	49.6 (0.0)	–	–	1.4	1.7
8 Jan. 2016	Rain on snow	4.9 (3.4)	–	–	3.1	4.2
30 Jan. 2016	Snowmelt	10.1 (5.4)	–	–	–	1.9
7 Feb. 2016	Rain on snow	4.5 (0.2)	–	–	–	1.6
18 Feb. 2016	Snowmelt	43.2 (15.9)	3.2	4.7	41.9	38.6
15 Mar. 2016	Rain	32.8 (0.0)	–	–	11.0	5.9
30 Mar. 2016	Rain	26.8 (0.0)	–	–	3.4	1.4
25 Dec. 2016	Rain on snow	29.6 (5.7)	–	–	0.4	0.5
10 Jan. 2017	Rain on snow	14.9 (3.7)	0.4	0.3	8.4	11.5
18 Jan. 2017	Rain on snow	23.8 (4.2)	7.5	20.9	10.3	5.4
20 Jan. 2017	Rain on snow	24.7 (5.7)	8.8	12.9	23.4	8.4
7 Feb. 2017	Snowmelt	13.8 (2.1)	–	–	4.3	1.6
11 Feb. 2017	Snowmelt	28.9 (8.3)	9.2	3.9	4.1	8.4
16 Feb. 2017	Snowmelt	12.7 (7.2)	–	–	0.4	–
20 Feb. 2017	Rain	30.0 (5.2)	–	–	0.3	0.3
28 Feb. 2017	Rain	29.4 (0.0)	–	–	0.3	0.6

after the January manure application were much greater than for the first event after the December application. This meant relatively more manure P mobilized by rain and snowmelt moved in runoff. Runoff dissolved P from NT plots after the January manure application was high for three events before decreasing substantially for the last two events (Fig. 3). Conversely, for the one runoff event on 18 February from CT plots after the January application, runoff P (0.96 mg L^{-1}) was about four times less than that from NT plots

(4.36 mg L^{-1}). Assuming that manure P availability was similar for both CT and NT plots for this event, less runoff P from CT plots is most likely due to less runoff (3–5 mm vs. 40 mm for NT plots, Table 1) and a subsequently lower runoff ratio.

For the December 2016 manure application, dissolved P in the first runoff event from NT plots (0.64 mg L^{-1}) was less than in the next three events ($\sim 3\text{--}5 \text{ mg L}^{-1}$) (Fig. 3). Thereafter,

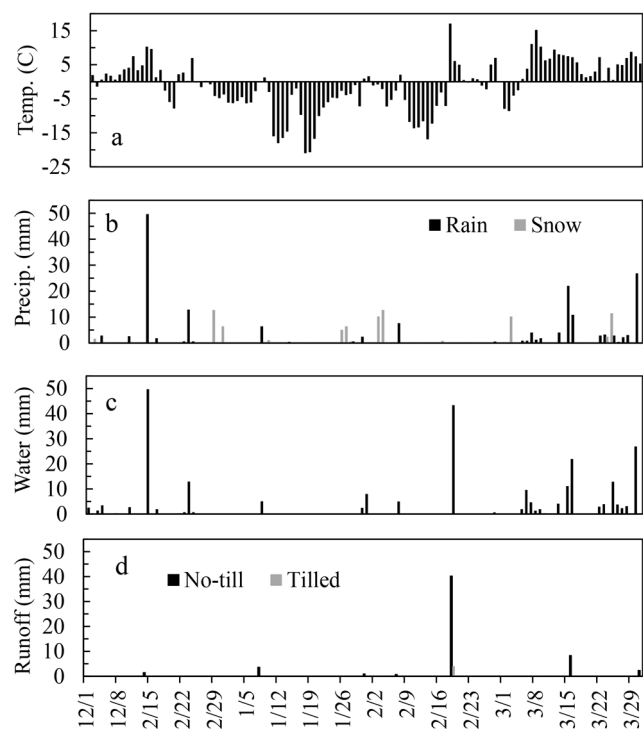


Fig. 1. (a) Air temperature (temp.), (b) precipitation (precip., rain and snow), (c) estimated amount of water from rain + snowmelt, and (d) runoff from chisel-tilled and no-till plots during the 2015–2016 winter monitoring period.

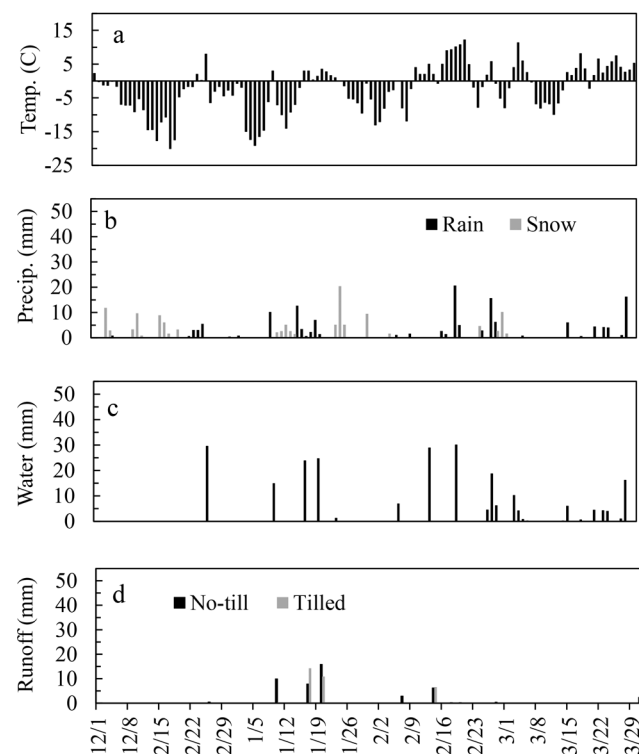


Fig. 2. (a) Air temperature (temp.), (b) precipitation (precip., rain and snow), (c) estimated amount of water from rain + snowmelt, and (d) runoff from chisel-tilled and no-till plots during the 2016–2017 winter monitoring period.

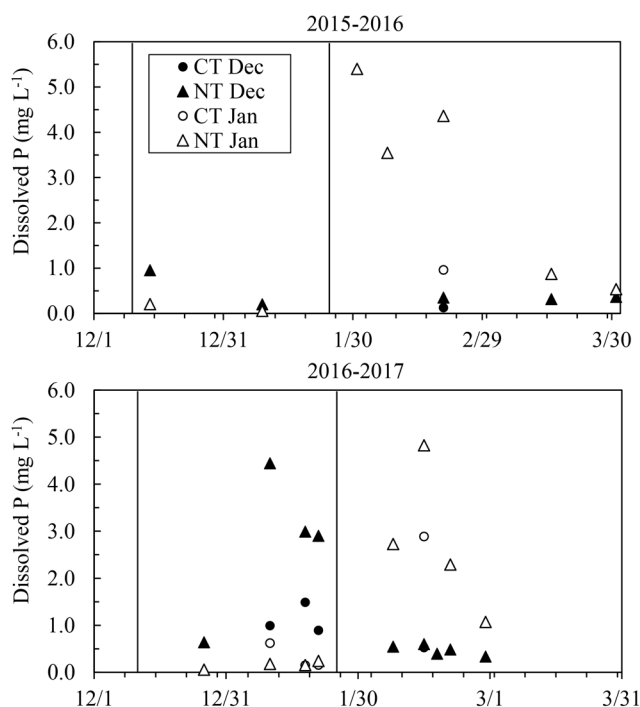


Fig. 3. Dissolved P concentrations in runoff from chisel-tilled (CT) and no-till (NT) plots receiving liquid dairy manure in either December or January during both the 2015–2016 and 2016–2017 winter monitoring periods. Vertical lines indicate dates of manure application.

runoff dissolved P was much less (average of 0.47 mg L^{-1}) and closer to control plot concentrations (average of 0.15 mg L^{-1}) (Fig. 3). These trends are consistent with data from the previous year for high runoff P in early events after application and decreased runoff P in later events. However, the first event had the least runoff P of the first four events. This is likely due to a low runoff ratio for this event (0.02, $\sim 26 \text{ mm}$ of rain and snowmelt water and 0.4 mm of runoff) compared with the next three events (runoff ratios of 0.45 to 0.84) (Table 1). It may also be due to a lower than typical rate of manure P release by snowmelt water compared with what we have observed for other manures in our research (see Vadas et al., 2018, and discussion about SurPhos modeling assumptions below). For the December 2016 application on CT plots, runoff did not occur until 10 January, and runoff dissolved P for this and the next two events (average of 0.97 mg L^{-1}) was three to four times less than runoff P from the NT plots for the same dates (Fig. 3). As we proposed for the 2016 January manure application, this is most likely due to less runoff from CT plots ($0.4\text{--}9 \text{ mm}$ vs. $8\text{--}23 \text{ mm}$ from NT plots, Table 1) and subsequently lower runoff ratios. Dissolved P in runoff was much less from both CT and NT plots after the end of January, reflecting reduced P availability in manure after 2 to 3 mo of exposure to rain and snowmelt.

Overall, runoff P concentrations for the December manure application were much greater in 2016–2017 than in 2015–2016, most likely because the 2016–2017 application was on top of snow instead of onto bare, unfrozen soil. This allowed manure liquid to remain in the snowpack and leave more manure P available for loss in runoff. In fact, the greatest runoff P concentrations for the 2016 December manure application were similar to those for the 2016 January manure application, which was also applied on top of snow.

After the January 2017 manure application, dissolved P was relatively high in the first three runoff events from NT plots ($\sim 2\text{--}5 \text{ mg L}^{-1}$) before decreasing in the last event (1.07 mg L^{-1}) (Fig. 3). For the January application on CT plots, runoff P in the only event (14 Feb. 2017, 2.89 mg L^{-1}) was less than runoff P from the NT plots (4.82 mg L^{-1}). Assuming that manure P availability was similar for both plot types, differences in runoff P are likely due to less runoff from CT plots (3.9 mm) than from NT plots (8.3 mm) and a lower runoff ratio. Overall, magnitudes of runoff P concentrations in the first events after the January application were similar to the other two manure applications on top of snow (January 2016 and December 2016).

The above presentation of dissolved runoff P data highlights how hydrology (specifically the runoff ratio) can influence manure runoff P concentrations. To investigate this, we compared hydrology and runoff P data pairs, where a pair consisted of runoff events on the same date for both CT and NT plots that had manure applied at the same time. For example, one pair was for the 20 Feb. 2016 event from both CT and NT plots after the January application. There were eight such data pairs across the two winters. For each pair, we calculated the runoff ratio for both CT and NT plots and then divided the lesser ratio by the greater ratio (CT plots had a lesser ratio in all but one event). We then divided the runoff P concentration from the corresponding lesser ratio by the runoff P concentration of the greater ratio. We then plotted these relative runoff ratios and the relative runoff P concentrations for all eight data pairs. For resulting data in Fig. 4, there was a good correlation showing that relative runoff P increased as relative runoff ratios increased. This is because more rain + snowmelt water is moving in runoff rather than infiltrating into soil and carrying P mobilized from manure in runoff. Because the relationship was consistent across a number of runoff events at different times after manure application, hydrology likely has a greater influence on manure P runoff concentrations than timing of runoff relative to manure application (Vadas et al., 2011).

SurPhos Simulations

We have proposed that the runoff dissolved P dynamics described above are largely the result of three drivers, which are (i) manure P availability, as represented by both initial P content of applied manure and if liquid manure is applied onto snow, (ii) how much P is mobilized out of manure by rain and snowmelt water, and (iii) the hydrology of the runoff event as represented by the runoff ratio. To explore the validity of our proposed mechanisms, we simulated our experimental conditions with SurPhos, since the model simulates these processes. Reliably simulating dissolved P concentrations in runoff for our winter conditions would suggest that the mechanisms in SurPhos (which are consistent with those proposed in our discussion above) are the ones controlling manure P loss in runoff. We note that if liquid manure is applied ($<15\%$ solids), SurPhos assumes that 60% of manure P infiltrates into soil and is unavailable for direct loss in runoff. In this research, we maintained this assumption when liquid manure was applied to bare soil but eliminated it when manure was applied on top of snow.

Figure 5 shows measured and simulated data for runoff dissolved P from our field project ($n = 39$). The regression slope relating measured and predicted values was significantly greater

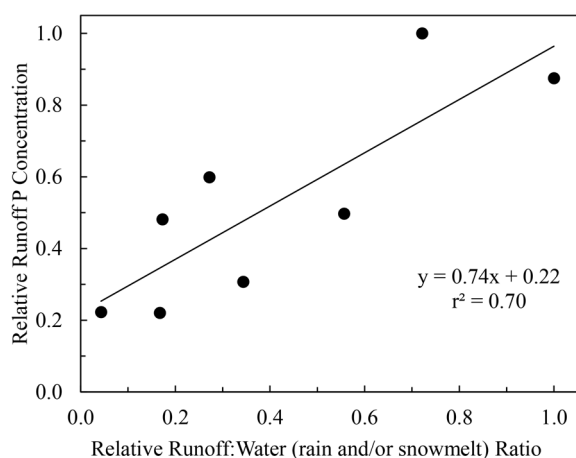


Fig. 4. Data from seven events after manure application when runoff occurred from both chisel-tilled (CT) and no-till (NT) plots. Regression lines show the relationship between relative runoff nutrient concentration and relative runoff ratios for the events.

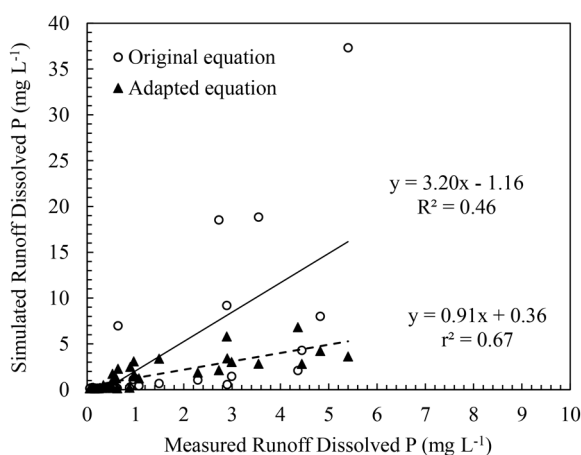


Fig. 5. Measured and SurPhos-simulated dissolved P concentrations in runoff for the field runoff data. Data represent model results for both the original SurPhos Eq. [1] for manure P release during snowmelt, and an adapted Eq. [2] particular to the dairy manure used in the field study.

than 1.0, but the intercept was not different from 0.0 ($p = 0.05$). The NSE was -17.48 , the RMSE was 6.43 mg L^{-1} , and the RSR was 4.24 , which do not suggest reliable P loss predictions. Visual inspection shows five points were highly overpredicted. Four of the points were for the first runoff event after manure application onto snow (30 Jan. 2016, 25 Dec. 2016, 7 Feb. 2017, and 11 Feb. 2017) and one point was the second event after the 30 Jan. 2016 event (7 Feb. 2016). SurPhos uses the following equation to estimate WEP release from manure during a rain or snowmelt event:

$$\text{WEP}_i \text{ released} = \{1.2[W/(W + 73.1)]\}(\text{manure WEP}_i) \quad [1]$$

where W is the ratio of water volume (rain and/or snowmelt) to manure mass ($\text{cm}^3 \text{ g}^{-1}$). In laboratory experiments using the liquid dairy manure from the same source as used in the field study, Vadas et al. (2018) found that Eq. [1] greatly overpredicted WEP release at lower W values (<150). The W values for the five events overpredicted ranged from 45 to $148 \text{ cm}^3 \text{ g}^{-1}$. Therefore, we assumed that Eq. [1] was overestimating WEP release from manure and causing overestimations of P concentrations in runoff. To account for this, we developed the following equation

to predict WEP release from the liquid manure used in the field study based on data from Vadas et al. (2018):

$$\text{WEP}_i \text{ release} = [0.0000144(W)^{2.029}](\text{manure WEP}_i) \quad [2]$$

Using Eq. [2] in the model instead of Eq. [1], the five overpredicted runoff P points decreased by an average of 14.8 mg L^{-1} (range in decrease from 3.3 to 33.7 mg L^{-1}), whereas all other prediction points increased by an average of 0.52 mg L^{-1} (range from decrease of 3.8 to increase of 4.7 mg L^{-1}). Compared with Eq. [1], Eq. [2] essentially allowed less manure P release during early runoff events after application, which generally left more P in manure for release in later events. Overall, new runoff dissolved P predictions greatly improved (Fig. 5). The new regression slope relating measured and predicted values was not significantly different from 1.0, and the intercept was not different from 0.0 ($p = 0.05$). The new NSE was 0.55, the RMSE was 1.00 mg L^{-1} , and the RSR was 0.66. Moriasi et al. (2007) provide guidelines for watershed-scale model performance for monthly time-step data based on NSE and RSR and would classify our NSE and RSR as satisfactory (NSE > 0.50 is satisfactory, and RSR between 0.60 and 0.70 is satisfactory). In other research evaluating the SurPhos model (Vadas et al., 2007, 2017; Wang et al., 2018), there has never been a need to use an alternative to Eq. [1], which suggests that the use of Eq. [2] was particular to only this liquid manure used in the field study.

Overall, our model performance statistics suggest SurPhos was reliably simulating dissolved P in runoff from manure for these winter conditions. This, in turn, suggests that the SurPhos manure P availability (i.e., liquid manure P remains completely available in the snowpack when applied on top of snow) and hydrology (i.e., the amount of rain and snowmelt water available to release WEP from manure and the amount of runoff as represented by the runoff ratio) processes are indeed the ones that control manure dissolved P loss in runoff. From a management and policy perspective, this means that dissolved P loss from manure applied in winter is a function of seasonal hydrology conditions and not the month that manure was applied. For example, manure applied in December may have as much risk of P loss in runoff as manure applied in February if the runoff hydrology is similar. Using the SurPhos model, Vadas et al. (2017) explored the long-term risk of dissolved P loss from manure applied during different days of the year. Similarly, Fallow et al. (2007) proposed a risk assessment approach based on soil and snow cover conditions to find suitable days for winter manure application. From a policy perspective, combining these modeling approaches could be used to set guidelines about the dynamics of P loss risk from manure spreading in winter and what fall or springtime periods are most suitable for application. From a management perspective, however, our research suggests that producers should still plan on assessing specific snow and soil conditions at the time of manure application during winter in addition to following guidelines about the risk of P loss in any given winter month.

Summary

Winter and early spring is consistently a time when significant runoff occurs from agricultural fields due to rain and snowmelt events on frozen soils. Therefore, winter application of dairy manure can greatly increase the risk of P loss in that runoff

relative to other times of the year. Understanding the hydrologic and soil frost conditions that control winter manure P loss can help develop management guidelines or application policies that can consistently reduce P runoff. Our results from winter runoff monitoring over 2 yr show that weather, soil frost conditions, and runoff timing and hydrology can vary greatly. However, there were consistent processes that controlled manure dissolved P runoff. For example, if liquid dairy manure can be applied onto bare, unfrozen soil, the manure liquid will have a chance to infiltrate into soil and reduce P available for loss in runoff. Liquid manure application on top of snow allows manure liquid to remain in the snowpack and increase P available to runoff. When runoff does occur, it is the runoff hydrology (as represented by both the amount of water available to release P from manure and the runoff ratio) that will control manure P concentrations in runoff. Therefore, management practices that can increase winter water infiltration can help reduce both runoff P concentrations and loads. We observed that fall tillage helped to create surface roughness that increased water infiltration into soil and decrease runoff P concentrations. However, such tillage to increase winter water infiltration would have to be balanced with practices that help decrease soil erosion in other parts of the year that might occur due to fall soil disturbance. Our results also show that timing of manure application is not a reliable practice for reducing manure P in runoff. For example, risk of P loss in the first runoff events after a December manure application on top of snow can be just as high as that from a similar January or February application. Therefore, if winter manure applications need to occur, they should be before snow cover or before significant soil frost develops and onto a rough soil surface that can promote depressional water storage and infiltration. Finally, the SurPhos model is a tool that can be reliably used to explore and guide realistic expectations of the extent of P loss for different management and policy scenarios.

Conflict of Interest

The authors declare no conflict of interest.

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