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# Nitrogen, Phosphorus, and Snowmelt Runoff Losses after Application of Dairy Manure with Variable Solids Content

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**Abstract:** Snowmelt nutrient loss is an important but poorly understood process in cold climates. We measured nutrient losses at three sites after dairy manure was applied on top of an established snowpack. Treatments included no manure controls and three manure solids levels (12–19.4% solids = High; 7.5–8.0% = Medium; 2.9–5.5% = Low) applied at 26,670 L ha$^{-1}$ to all treatments. Snowmelt runoff was monitored and analyzed for dissolved reactive P (DRP), total P (TP), total N (TN), ammonium-N, organic-N, and total solids (TS) concentrations. Results showed that manure application dramatically increased N and P loading compared to controls. Across site-years, manure application increased average runoff TP, DRP, and TN concentrations by 1.3- to 13.3-fold, 1.5- to 21-fold, and 1.4- to 14.2-fold, respectively, relative to controls. While cumulative N, P, and TS losses generally increased with manure solids, Medium/Low showed equal or greater nutrient transfer to runoff for some events. TN and TP lost in runoff were linearly related to manure solids concentration; however, N and P loss as a percent of applied showed the opposite trend. The results indicate that applying manure on top of snow resulted in high nutrient losses when runoff occurred regardless of manure solids content.

**Keywords:** dairy systems; manure; snowmelt; nutrients; surface runoff; water quality



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## 1. Introduction

Loss of nitrogen (N) and phosphorus (P) in surface runoff from manure and fertilizer applications represents an economic loss to farms and can contribute to water quality deterioration. Manure applied to fields during winter is particularly vulnerable to transport since snowmelt runoff often occurs on frozen soils when there is minimal infiltration potential. Reducing erosion potential and seasonal runoff nutrient losses from farm fields are both important for reducing nutrient loss to surface runoff water [1–3].

The U.S. dairy industry faces increasing pressure to improve on-farm nutrient use efficiency while decreasing environmental impacts [4]. In many areas of the Northern U.S. and Canada, dairy manure is routinely applied during the winter months due to logistical constraints (storage/time limitations) and sometimes performed after soils are frozen to reduce soil compaction risk [5,6]. Snowmelt runoff can comprise a substantial fraction of annual runoff flows in cold climates [3,7–9].

Soil and management factors (manure/tillage, cropping system, and nutrient management methods) affect both growing season and winter nutrient runoff losses. However, applying manure without any incorporation or on top of snow can have an overriding effect on N and P loss [10–13]. Research has clearly demonstrated that surface-applied manure (i.e., broadcast application) is much more vulnerable to transport in runoff compared to incorporated manure [9,14,15]. Winter nutrient loss from manure application can be exacerbated by a lack of vegetation, frozen soils, and greater runoff risk [9,12,16]. In addition to specific field and weather conditions, manure physico-chemical properties also affect nutrient losses when applied to soils during the growing season and snow/frozen soil conditions [5,17,18].

In addition to hydroclimatic factors, snow conditions, manure type/amount, and application timing/placement can also influence the melting process itself and nutrient losses [18–20]. Small plot and edge-of-field studies generally indicate greater loss risk when manure is applied directly on the snowpack as compared to fall application before snow accumulation, with late winter application resulting in particularly high nutrient losses [12,18–25]. Reduced nutrient losses with fall tillage before winter manure application has also been reported, presumably due to an increase in surface roughness [20,22,26], but this may be less effective with higher amounts of winter precipitation [20] or if overland flow occurs on non-frozen soil [24].

Manure type, timing, application rate, and method are all important considerations along with weather and field conditions for reducing nutrient losses to surface runoff [21,27]. Liquid (<12% solids content) versus semi-solid manure types can additionally affect loss potential and nutrient mobility with meltwater. Studies suggest that liquid manure may mobilize more readily than semi-solid manure types during snowmelt [22,23,28]. Both N and P mobility to overland flow are influenced by manure solids content and regulate water-extractable P release [19]. The SurPhos model [29] is one of the few models that accounts for the interaction between manure solids and meltwater to predict daily P loss in runoff. With 108 site-years of data, SurPhos predicted that wintertime dairy manure application increased runoff P losses from 2.5- to 3.6-fold relative to manure applied in the growing season [12].

Studies focused on manure nutrient losses under snowmelt conditions are relatively rare, hindering the development and validation of modeling programs accounting for winter nutrient losses [16]. Even fewer recent studies include both N and P loss dynamics after applying manure to a snowpack. An improved understanding of nutrient dynamics from winter-applied manure will support the development of new N and P loss tools and provide sound field data for revising nutrient management guidelines in cold climates [3,5,16,18–25]. Here, our objective was to quantify event-based and cumulative snowmelt runoff flows and losses of N (ammonium-N and organic-N) and P (TP, DRP, and unreactive-P) at three sites in the upper Midwest after a one-time application of dairy manure varying in total solids content was applied on top of the snowpack.

## 2. Materials and Methods

Vadas et al. [19] reported that lower solids content dairy manure (3.7%) had greater meltwater dissolved reactive phosphorus (DRP) compared to applying higher solids (14.9%) manure (and more total P) in a laboratory study. We wished to test if similar results occur at the field scale, and an initial trial was therefore conducted at the University of Wisconsin Arlington Research Station in 2017, and only DRP in snowmelt runoff was analyzed (Table 1). A second trial was conducted in 2018 at Arlington. Similar experiments were carried out at the University of Minnesota in 2018 and 2019. Only High (19.7%) and Low (2.9%) manure solids treatments were included in addition to controls (no manure) at Minnesota due to a limited number of plot samplers. An additional experiment was also conducted in 2019 at USDA-ARS' Institute for Environmentally Integrated Dairy Management Research Unit in Marshfield, Wisconsin (Table 2). There were three levels of manure solids content (High, 15.4%; Medium, 8.0%; and Low, 5.5%). For Minnesota and Marshfield, snowmelt runoff, solids, N (total N, ammonium-N, organic-N), and P (total P, DRP, particulate P) concentrations/loads were measured for each event. For the Arlington site, DRP was measured in 2017 while DRP, ammonium-N, and nitrate-N were measured in 2018.

**Table 1.** Manure composition and estimated total nitrogen and phosphorus applied.

| Treatment | Manure Composition | | | Nutrients Applied | |
|---|---|---|---|---|---|
| | Solids Content | TN | TP | TN | TP |
| | % | | | kg/ha | |
| Arlington, Wisconsin 2017 and 2018 | | | | | |
| High | 14.9 | 2.89 | 1.01 | 141 | 49.3 |
| Medium | 7.5 | - | - | 70.4 | 24.7 |
| Low | 3.7 | - | - | 35.2 | 12.3 |
| St. Paul, Minnesota 2018 | | | | | |
| High | 19.7 | 2.14 | 1.35 | 138 | 87.1 |
| Low | 2.9 | 1.62 | 1.81 | 15.3 | 17.2 |
| St. Paul, Minnesota 2019 | | | | | |
| High | 14.6 | 2.65 | 1.04 | 130 | 51.1 |
| Low | 3.0 | 2.80 | 1.07 | 27.5 | 10.5 |
| Marshfield, Wisconsin 2019 | | | | | |
| High | 15.4 | 3.00 | 1.11 | 129 | 47.8 |
| Medium | 8.0 | 2.90 | 1.02 | 64.9 | 22.8 |
| Low | 5.5 | 2.70 | 1.02 | 41.5 | 15.7 |

Note: Only the High manure solids treatment was analyzed for the Arlington trial. Total P and N for Medium and Low manure treatments were based on dilution of the High sample.

**Table 2.** Average concentrations by treatment for each site and year.

| Variable | Control | Low | Medium | High |
|---|---|---|---|---|
| Arlington Station, Wisconsin (2017) | | | | |
| DRP | 0.23 $^{a}$ | 3.8 $^{b}$ | 4.9 $^{bc}$ | 2.9 $^{b}$ |
| Arlington Station, Wisconsin (2018) | | | | |
| DRP | 0.59 $^{a}$ | 2.1 $^{b}$ | 3.7 $^{c}$ | 4.8 $^{d}$ |
| Ammonium-N | 0.56 $^{a}$ | 1.7 $^{a}$ | 2.6 $^{b}$ | 3.3 $^{b}$ |
| University of Minnesota (2018) | | | | |
| DRP | 0.48 $^{a}$ | 4.1 $^{b}$ | — | 4.2 $^{b}$ |
| Total P | 0.61 $^{a}$ | 6.3 $^{b}$ | — | 8.1 $^{b}$ |
| PUP | 0.15 $^{a}$ | 2.2 $^{b}$ | — | 3.8 $^{b}$ |
| TS | 166 $^{a}$ | 318 $^{b}$ | — | 788 $^{c}$ |
| Ammonium-N | 0.81 $^{a}$ | 6.0 $^{b}$ | — | 21.0 $^{c}$ |
| Total N | 2.5 $^{a}$ | 11.9 $^{b}$ | — | 35.6 $^{c}$ |
| Organic-N | 1.3 | 1.1 | — | 4.8 |
| University of Minnesota (2019) | | | | |
| DRP | 0.39 $^{a}$ | 0.82 $^{b}$ | — | 3.6 $^{c}$ |
| Total P | 0.79 $^{a}$ | 1.4 $^{a}$ | — | 8.1 $^{b}$ |
| PUP | 0.36 $^{a}$ | 0.61 $^{a}$ | — | 1.7 $^{b}$ |
| TS | 279 $^{a}$ | 447 $^{b}$ | — | 362 $^{ab}$ |
| Ammonium-N | 0.71 $^{a}$ | 1.4 $^{a}$ | — | 5.6 $^{b}$ |
| Total N | 2.4 $^{a}$ | 5.3 $^{b}$ | — | 10.6 $^{c}$ |
| Organic-N | 1.1 a | 3.1 $^{b}$ | — | 4.2 $^{b}$ |
| Marshfield Station, Wisconsin (2019) | | | | |
| DRP | 0.62 $^{a}$ | 0.9 $^{a}$ | 1.4 $^{a}$ | 3.0 $^{b}$ |
| Total P | 1.7 $^{a}$ | 2.2 $^{a}$ | 3.2 $^{b}$ | 6.3 $^{b}$ |
| PUP | 1.1 $^{a}$ | 1.3 $^{a}$ | 1.8 $^{a}$ | 3.3 $^{b}$ |
| TS | 2196 $^{a}$ | 859 $^{b}$ | 487 $^{b}$ | 804 $^{b}$ |
| Ammonium-N | 0.63 $^{a}$ | 1.1 $^{b}$ | 1.6 $^{b}$ | 3.0 $^{b}$ |
| Total N | 5.6 $^{a}$ | 7.6 $^{a}$ | 9.2 $^{a}$ | 21.2 $^{b}$ |
| Organic-N | 3.9 | 5.2 | 6.2 | 16.5 |

Note: Concentrations without a common lower case letter differ ($p \leq 0.05$). Values without any lower case letters indicate that no significant ($p \geq 0.05$) differences were detected.

Specialized snowmelt samplers were installed in corn fields in late fall/early winter prior to snow accumulation and the onset of soil freezing. Sites were located on actively managed cropland associated with university farms. Soils at the Arlington Station were mapped as the well-drained Plano silt loam series (fine-silty, mixed, superactive, mesic Typic Argiudolls), classified as a Mollic Anthrosol (Anosiltic, Cutanic, Differentic, Luvic) using the World Reference Base for Soil Resources criteria [30]. The University of Minnesota trials were performed in a corn silage field mapped as a well-drained Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludolls; approximately 5% slope), classified as a Mollic Anthrosol (Anosiltic, Cambic, Cutanic, Differentic, Luvic) [30]. The trial at the Marshfield Station was performed in a grain corn field mapped as the somewhat poorly drained Withee silt loam (fine-loamy, mixed, superactive, frigid Aquic Glossudalfs; 1–3% slope), classified as a Gleyic Anthrosol (Anosiltic, Cutanic, Differentic, Luvic, Ochrich) [30].

Experiments were set up as randomized complete block designs with 3 blocks and 4 treatments (Wisconsin) or 3 blocks and 3 treatments (Minnesota). Each plot consisted of an individual snowmelt runoff sampler installed in a line perpendicular to the field slope, with approximately 1 to 1.5 m between each frame to allow for access around all sides. Frames were fabricated from thin-walled aluminum sheets (99 cm length, 49.5 cm width, and 25.5 cm height) equipped with V-shaped outlets connecting to a 3 m long, 5 cm diameter PVC outlet drainage pipe (Figure 1). Frames were installed in the fall by inserting approximately 2.5 cm into the soil (a wire mesh screen was placed in the outlet as an animal guard).

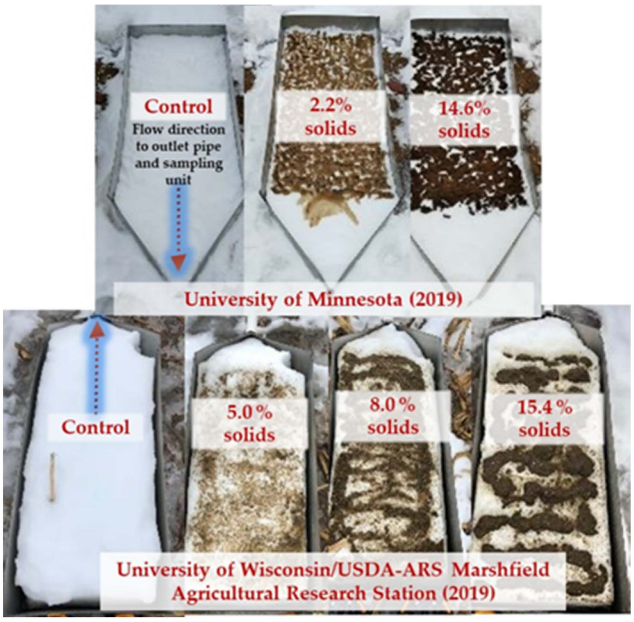


**Figure 1.** Photographs showing snowmelt runoff plots after manure application for the University of Minnesota and Marshfield Station (2019).

At the Arlington and Minnesota locations, pipes drained into 19 L buckets located inside 38 L aluminum garbage cans fitted with a rubber gasket to hold the pipe in place in the wall of the can and a tight fitted lid to exclude outside precipitation or other contamination sources. These cans were buried halfway in the soil so the pipe entrance to the can was at soil surface elevation to maintain a downward slope. Buckets were removed and the amount of water was determined by weight or depth, and a sample was collected for analysis (250 to 1000 mL sample from each bucket was collected). For larger events, buckets were emptied as needed and sub-samples of equal volumes were combined for analysis. The setup at Marshfield was similar, except PVC pipes drained to 80 L polyethylene collection bags (Planit Products Ltd., Malvern, U.K.). Pipes were attached to bags using PVC fittings and the bags were wrapped in tarps with a PVC frame over the pipe connection to prevent snow buildup on the outlet, allowing free flow of liquid into the bag.

Fresh manure was collected from free-stall or tie-stall lactating cow barns at each experiment site, with each farm providing its own manure sample. Each site utilized manure produced from the university-associated farm where the field research was conducted (Table 1). Fresh manure collected from barns was considered the High manure solids treatment (14.6–19.7% solids). Medium treatments (7.5–8.0% solids) consisted of the High treatment diluted approximately in half with deionized water (both Wisconsin trials), and Low solids treatments (2.9–5.5%) were prepared by diluting fresh manure to 1/3 of the raw manure solids content. Manure was hand-applied at a rate of 26,670 L $ha^{-1}$ (1600 g/plot) across the snow surface (generally in late January to early March depending on weather). Select physical and chemical manure properties (total solids/dry matter, total N and P) were analyzed by the UW Soil and Forage Laboratory following established procedures [31]. Soil samples were collected (5 cores, 2 cm in diameter at 2.5 cm depth) around the immediate perimeter of the snowmelt runoff samplers for agronomic fertility assessment the previous fall. Cores were composited, air-dried, ground to 2 mm, and analyzed for Bray-1 extractable P (Peters, 2013). The Bray-1 extractant is used for Wisconsin and Minnesota nutrient guidelines. Average plot Bray-1 extractable P concentrations at the Minnesota ($112 \pm 16$ mg $kg^{-1}$) and Marshfield ($40 \pm 6$ mg $kg^{-1}$) sites were in the agronomic high range, where further P inputs from manure or fertilizer would be unlikely to increase crop yield potential.

Snowmelt runoff event samples were kept at 4 °C or frozen until analyses could be conducted. Samples were analyzed for total solids (TS) by gravimetric analysis (method 2540 B. [32]) and TN and TP by the persulfate/autoclave method [33]. A subsample (50 mL) was passed through a 0.45 µm pore size filter the day of collection, followed by analysis for DRP [34], $NO_3$-N [35], and $NH_4$-N [36] by automated flow injection analysis. We also evaluated the difference between TP and DRP, representing P bound to particulates and/or dissolved unreactive P (PUP). Loads for total solids and nutrients were calculated by multiplying event flow volumes by respective concentrations.

Snow depths and density cores were taken before and after select melting events to quantify snowpack density and water equivalent changes for the Marshfield and Minnesota trials. Snow core samples were taken with PVC pipe sections of known diameter and inserted into the snowpack (Marshfield and Minnesota sites) to the top of the soil surface near each frame. Snow depths were estimated with tape measures inserted into the same holes used for core samples. Snow in the cores was melted and mass was recorded. Density was calculated as mass per volume of each core. At the Arlington sites, snow depth in plots near the sampling units was periodically measured. Weather stations operated by the University of Minnesota and University of Wisconsin captured daily temperature and precipitation, and precipitation was also recorded by nearby weather stations. Site-specific weather and total precipitation (rain + snow) were compared to 30-year mean values for nearby weather stations to place site weather data into a broader climatic context.

Plots were arranged in a randomized complete block design at each site in active crop production fields. Normality for dependent variables was assessed (Proc Univariate) using the Kolmogorov–Smirnov statistic with a threshold for non-normality set at $p \leq 0.05$. The generalized mixed modeling procedure (Proc Glimmix) of the Statistical Analysis System [37] was used to assess the effect of manure solids content on nutrient loads and concentrations for individual snowmelt events and cumulative loads. Proc Glimmix handles normally and non-normally distributed dependent variables. Least square means for controls and manure solids treatments were separated using the SMM option in SAS. For non-normally distributed variables, gamma, inverse Gaussian, and Poisson distributions were used and selected based on meeting model convergence criteria. To gain insight on relationships among TS, TP, TN, and associated soluble forms, data from all site-years were pooled, and linear regression was performed on select variables (TS, TP, TN, ammonium-N, DRP, DRP/TP, inorganic-N/TN, and organic N and P).

## 3. Results and Discussion

### *3.1. Weather Conditions*

Mean monthly temperatures for the Arlington Station for the winter period of 2017 and 2018 were similar to 30-year averages (Dane County Regional Airport), except for April 2018, which was 7.3 °C cooler than the 30-year mean. Arlington had wetter than normal conditions in 2017 and drier than normal conditions in 2018. Winter 2018 temperatures for St. Paul, Minnesota were substantially cooler than normal for February and April (by 5.2 and 7.8 °C, respectively). In general, precipitation for St. Paul, Minnesota (2018 and 2019) and Marshfield (2019) was higher than 30-year means. Minnesota (2018 and 2019) and Marshfield had more snowfall than Arlington in either year (Supplementary Material Figure S1). In 2019, a large snowstorm in mid-March contributed most of the snowfall for the season at Marshfield. Average snow depths were periodically measured at each site over the monitoring periods (Supplementary Material Figure S1).

### *3.2. Snowmelt Runoff and Manure Application Impacts*

Timing/amounts of snowmelt runoff varied across sites (Figure 2). Minnesota (2018) and Marshfield (2019) had larger runoff flows compared Arlington and Minnesota (2019). Snowfall accumulated through much of the winter at the Minnesota site in 2018 (Supplementary Material Figure S1), with the first melt event on 29 January 2018 (day 0) and the last on 31 March 2018 (day 61). A large melting event occurred in late March 2018 with median runoff values of >50 mm/plot. In 2019, there was less snowfall with smaller events compared to 2018 (Figure 2). Arlington had less snowfall both years with correspondingly less runoff. At the Marshfield Station, a large winter storm occurred on 5 March 2018, accounting for most of the season's snow melting occurring between 15 March 2019 and 7 April 2019 (day 0 and day 33, respectively).

There were only a few events when manure significantly ( $p \leq 0.05$) affected snowmelt runoff quantity (Figure 2). The lack of significance is likely related to variability in snowpack densities and melting processes within/across treatments. High and Low manure solid treatments for Minnesota in 2018 had similar runoff amounts until later events (Figure 2). In 2019, the High treatment had consistently more snowmelt runoff than other treatments. At Marshfield, the Medium treatment had consistently more runoff than other treatments (Figure 2). There was less runoff variability among treatments at the Arlington Station for both years of monitoring, with few differences in either year. In contrast, Stock et al. [20] reported earlier melting for liquid dairy manure (2–6% solids) applied on top of snow at the Arlington Research Station that nearly doubled N and P losses compared to earlier before snow accumulation. We hypothesize that while manure could have altered thermal conditions and melting, it was difficult to determine the impact of manure on melting given other potentially confounding factors (i.e., snowpack density variation among plots). Collectively, our study showed no clear impact of manure altering snowmelt runoff hydrology.

### *3.3. Manure Effects on Dissolved Reactive Phosphorus Concentrations and Loads*

Mean DRP concentrations for Medium and Low manure solids treatments were over 200-fold greater than the control for the first melting event at Arlington in 2017 (Figure 3), decreasing sharply for subsequent events and similar to controls for the last event (Figure 3). In contrast to 2017 trends, 2018 DRP concentrations increased for subsequent events since the first melting event (Figure 3). There were significant main effects for the first three events in 2017, whereas in 2018, it was the last three events (Figure 3).

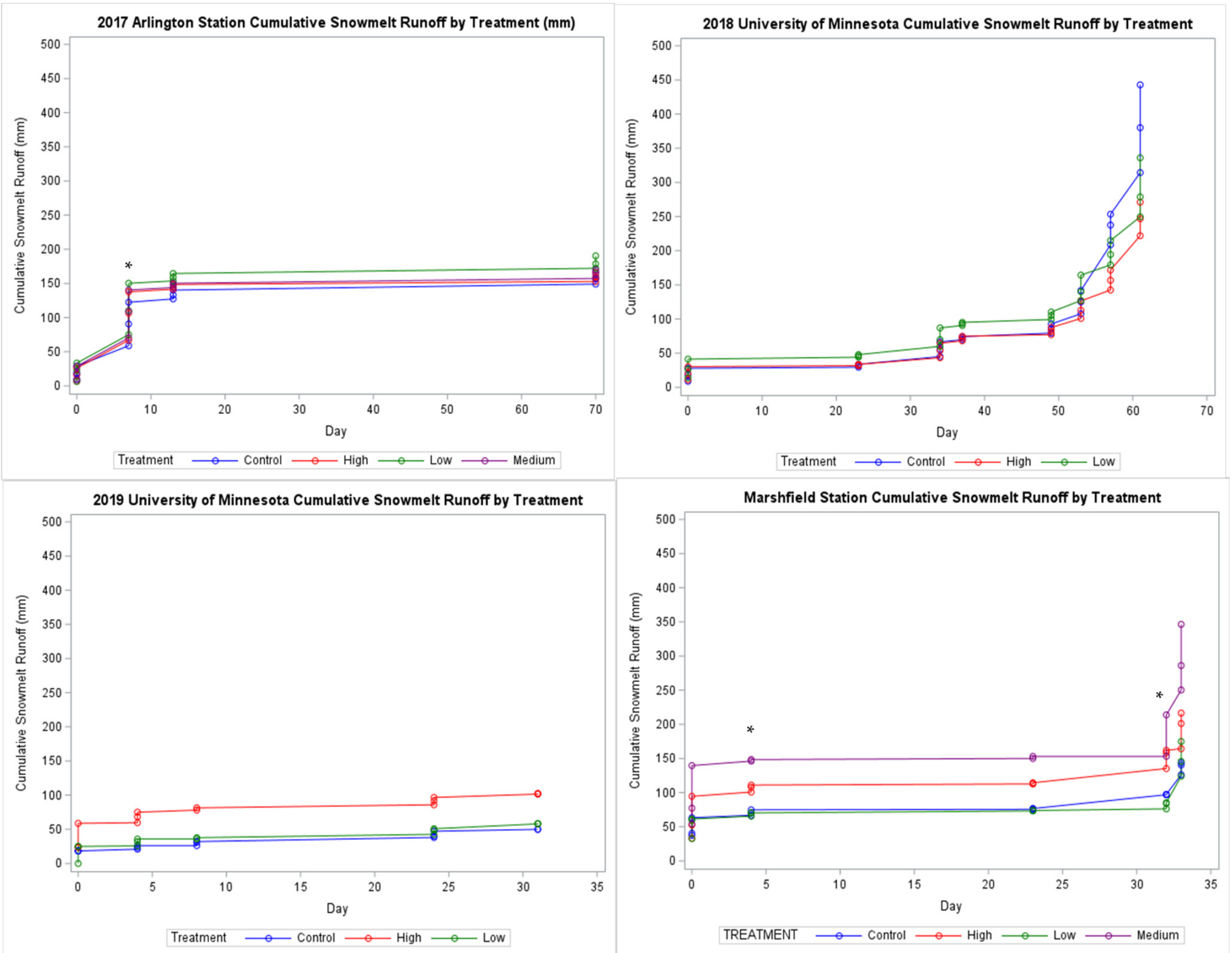


**Figure 2.** Cumulative snowmelt runoff by treatments for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids content on snowmelt runoff. The trial was conducted at the Marshfield Station for one year only in 2019.

Manure treatments at Minnesota substantially increased snowmelt DRP concentrations in both years compared to the control (Figure 3). For the first two events in 2018, DRP concentrations for the Low solids treatment were greater than the High, whereas the High treatment had greater DRP in the last two events (Figure 3). This pattern may suggest greater manure P mobilization from the High treatment with later melting events after manure solids presumably had more time for integration into the snowpack. In 2019, the High solids treatment had greater DRP concentrations for the first three events, with DRP decreasing sharply for subsequent events, suggesting that much of the DRP may have been mobilized by pervious events. At Marshfield, manure treatment DRP concentrations peaked for the first two events, declining sharply for the last three events with few differences (Figure 3).

Given variable snowpack conditions and DRP concentrations during melting, we also calculated mean DRP and other constituent concentrations across all events for each site-year as another way to compare average treatment effects (Table 2). Medium and High DRP concentrations did not differ significantly in 2017 for Arlington. In 2018, average event DRP concentrations among treatments also differed significantly and increased with manure solids application (Table 2). At Minnesota (2018), mean DRP concentrations were virtually identical between High and Low treatments, but in 2019, mean event DRP was more than 4-fold greater for the High treatment.

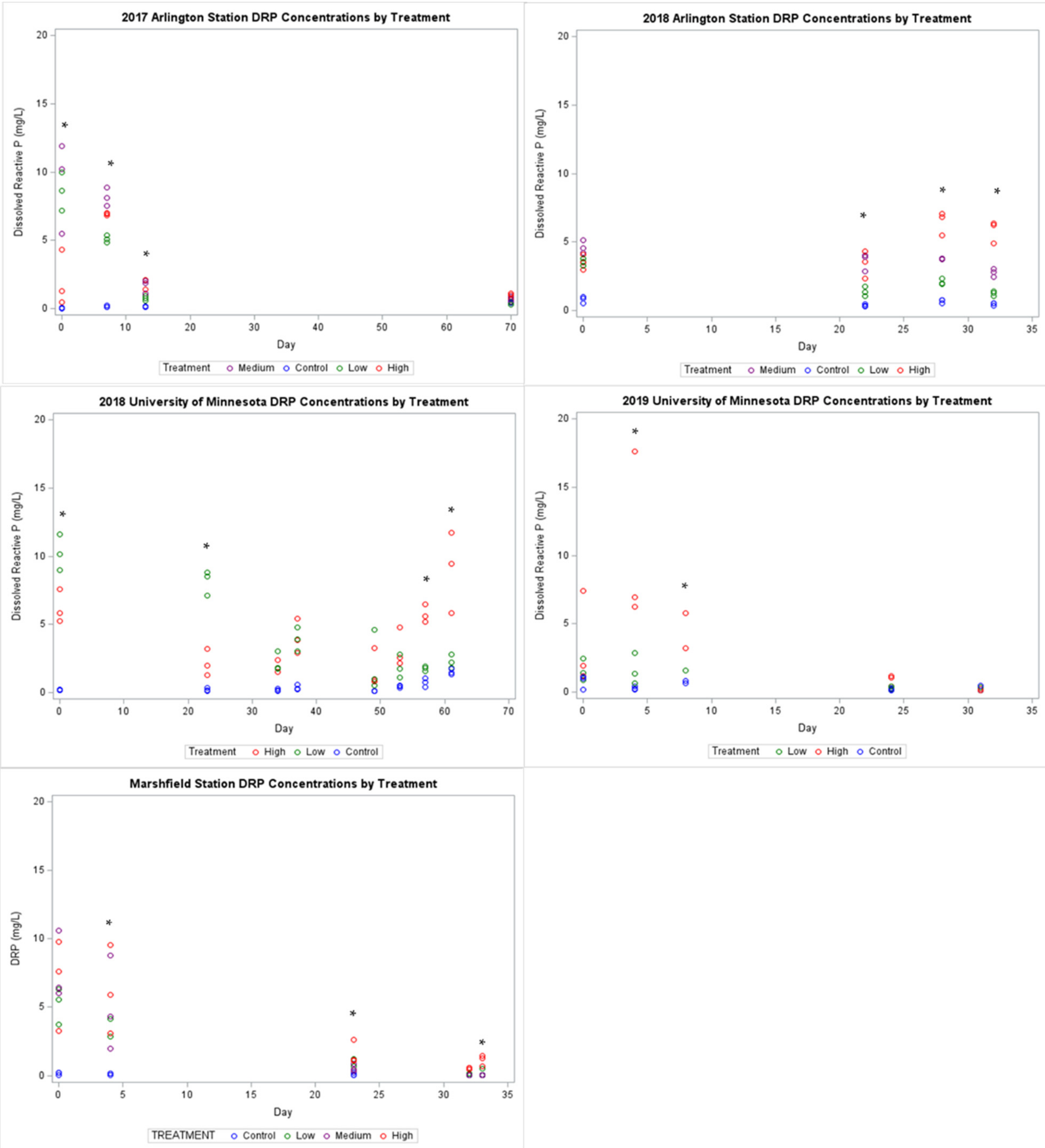


**Figure 3.** Dissolved reactive phosphorus (DRP) concentrations by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids content.

At Marshfield, the average High treatment DRP concentration was significantly greater compared to Medium, Low, or control (Table 2). In a laboratory assessment of manure nutrient leaching from snowmelt, Vadas et al. [19] showed that DRP from liquid manure was more vulnerable to transport with meltwater compared to semi-solid manure. While our results suggest that manure-P from Medium and Low treatments may have been more readily mobilized compared to the High solids treatment for a few events (mainly at Arlington), higher manure solid treatments generally had greater DRP concentrations and loads and was likely driven by the greater manure TP/DRP loads applied with the higher solids content manures compared to the more dilute, lower solids content manure

(Table 1). It is also important to note that Vadas et al. [19] was a laboratory-based study with liquid dairy manure applied on top of small volumes of snow placed in laboratory funnels, and therefore does not capture more complex interactions between meltwater and manure nutrients occurring at the field scale.

Manure treatment DRP loading trends were broadly similar to DRP concentration trends, but they were not always consistent due to high runoff variability at Marshfield and Minnesota (Figure 4 and Table 2). At Arlington, the Medium treatment had consistently greater event DRP loads and cumulative DRP loading in 2017 and greater DRP loading in 2018 until later events (Figure 4). A similar trend occurred at the Minnesota site in 2018 for Low and High treatments, with Low maintaining greater DRP loads until later melting events (Figure 4).

In 2019, DRP loads were consistently greater for the High treatment in Minnesota. A similar trend occurred at Marshfield, where the Medium treatment had consistently greater DRP loading after the first event (Medium also had the highest cumulative runoff). Based on cumulative losses across site-years, manure treatments increased DRP loads by an average of 3.2- to 44.8-fold compared to controls, indicating that manure applied on top of snow was a potent DRP source in snowmelt runoff.

Our findings indicate that DRP from dairy manure applied on top of snow was highly vulnerable to transport in snowmelt water runoff, despite a wide range of variation in solids content/liquidity and site conditions. Young and Mutchler [38] similarly reported high DRP concentrations and loads (<0.1 to 8.4 mg $L^{-1}$ and <0.1 to < to 4.8 kg $ha^{-1}$) in snowmelt runoff for corn and alfalfa plots in a Minnesota runoff study, with up to 16% of manure-applied P accounted for in runoff. In a 2-year winter runoff study at the Arlington Station with no-till and conventional tillage, Vadas et al. [22] showed that DRP and manure solids loss in runoff were larger when manure was applied on top of snow before a melting event, as manure remained in the snowpack to interact with meltwater during subsequent events. Komiskey et al. [21] reported their highest flow-weighted mean runoff TP concentration of 10.9 mg $L^{-1}$ (>80% in DRP form) when manure was applied less than one week before a melt event, stressing the importance of application timing in relation to snowpack and weather conditions.

Our study was designed to represent a high DRP-loss risk condition associated with applying manure on top of snow, what would generally be considered a "worst case scenario" for nutrient loss potential. While winter manure application is typically discouraged in many regions, it remains a routine practice despite few studies investigating winter N and P losses. It is important to place the high DRP concentrations/loads from our experiments into the context of larger field results. Our snowmelt runoff plots had open bottoms allowing infiltration should conditions permit, but otherwise were designed to maximize snowmelt water capture with little chance for DRP attenuation processes during transport, as would be more typical in a larger field setting. Since DRP is mainly orthophosphate and immediately bioavailable, the high DRP concentrations/loads measured in our experiments could be viewed as a high water quality risk condition, particularly if snowmelt runoff could be transported to nearby surface waters. We caution that our DRP load estimates may be high compared to edge-of-field or small paired watershed-type monitoring designs, where runoff is more of an integration of larger scale hydrologic processes (dilution/dispersion) that would likely further reduce loads and DRP concentrations in runoff before reaching surface waters.

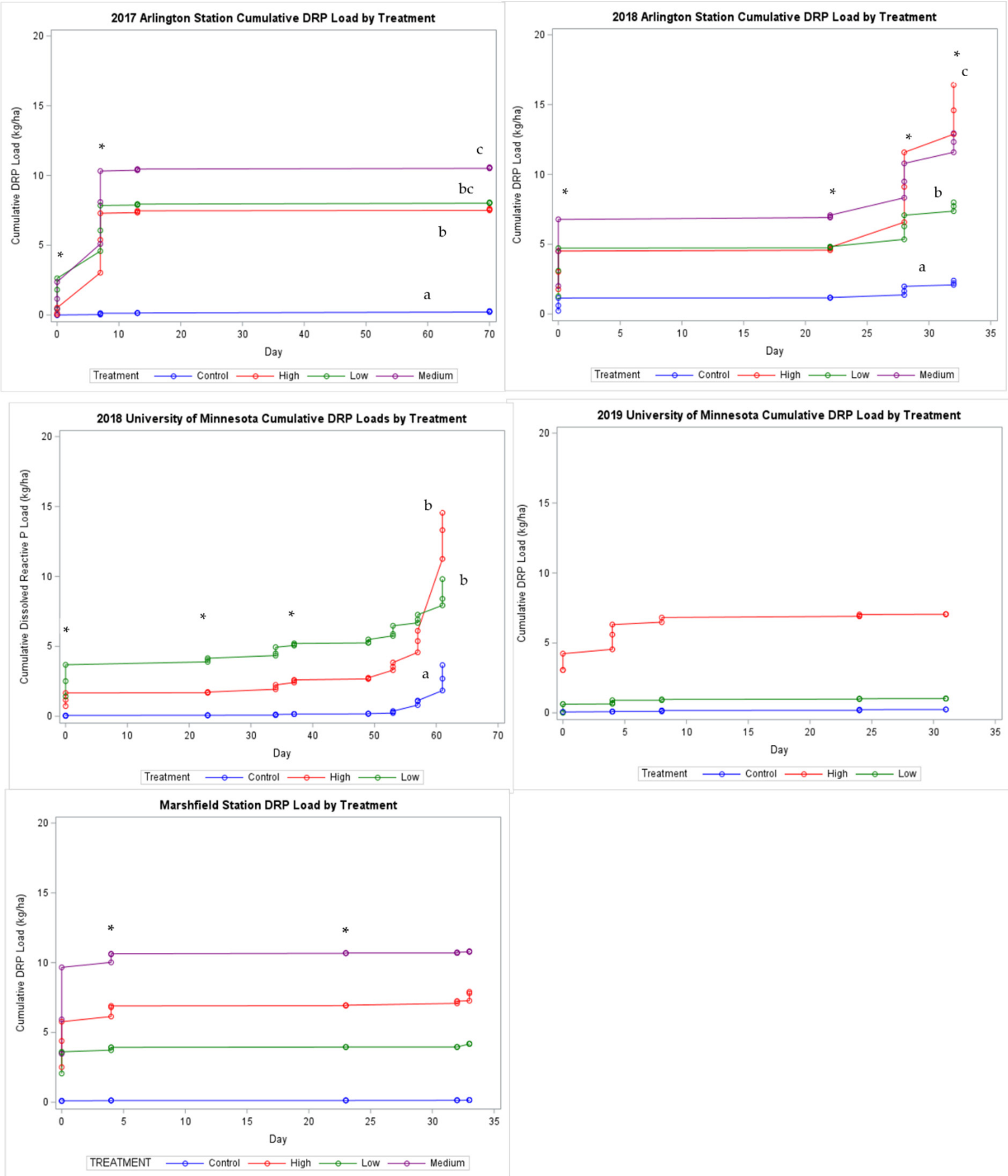


**Figure 4.** Event and cumulative dissolved reactive phosphorus (DRP) loading by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids. Cumulative loads without a common lower case letter differ ($p \leq 0.05$).

### *3.4. Total Phosphorus and Total Solids*

TP loss trends were similar to DRP with respect to treatment response and monitoring year impacts (Figure 5). Manure treatment snowmelt TP concentrations peaked at the first or second event for Minnesota both years and for the Marshfield Station, decreasing substantially thereafter. This suggests a "flushing" effect of manure P from the snowpack and/or dilution with additional melting episodes. The large DRP load increase observed during the last several melting events in 2018 was also evident for TP. During this time, TP loads increased sharply for the High treatment, surpassing cumulative TP loading for the Low treatment by approximately 10 kg ha$^{-1}$ (Figure 5).

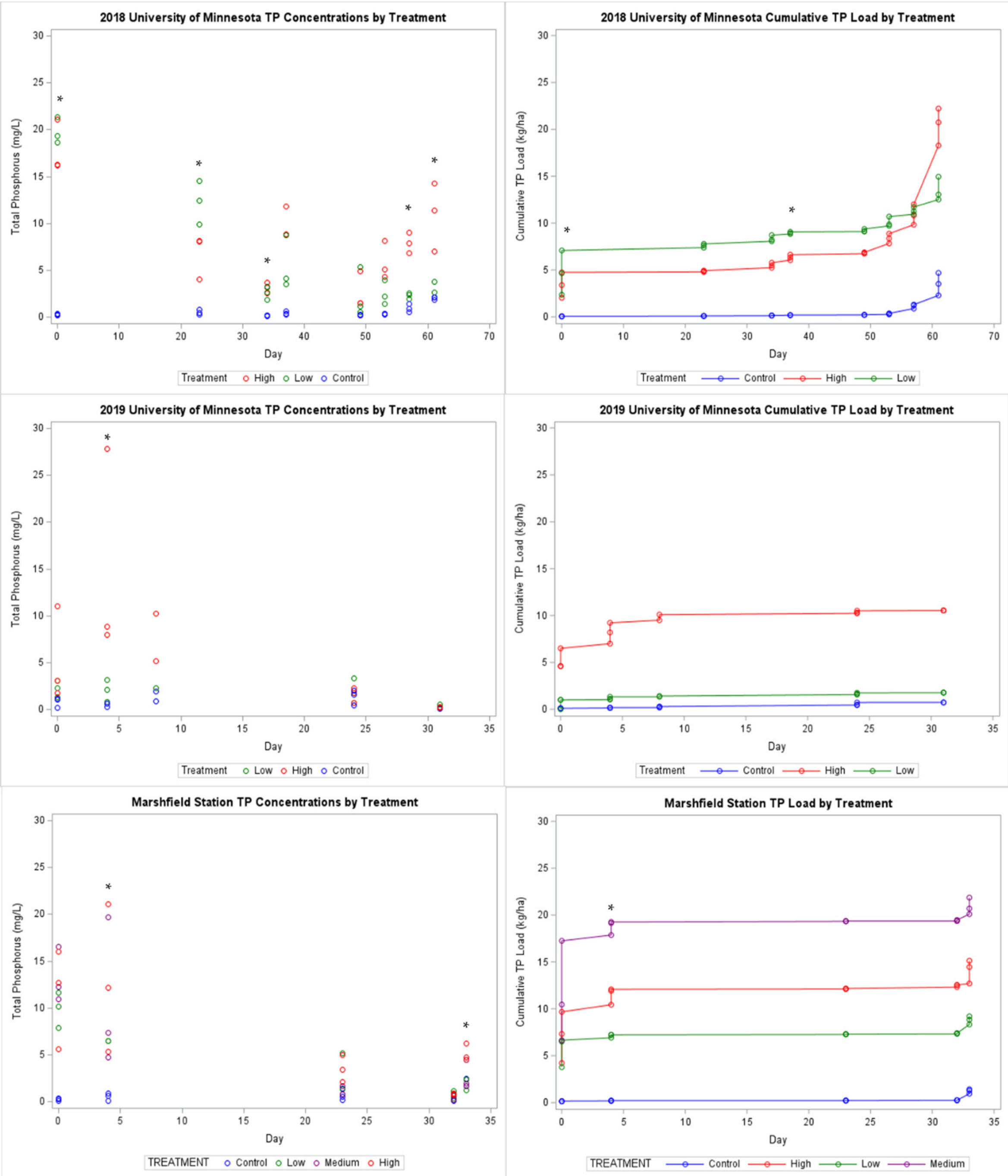


**Figure 5.** Snowmelt runoff total phosphorus (TP) concentrations/loads by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids.

The rapid increase in cumulative TP was likely related to a change in snowpack hydrology with increased interaction between manure solids and meltwater likely mobilizing additional manure-P from the High treatment. Again, this is likely due to the fact that much more TP was applied for the High treatment (Table 1). Average event TP concentrations at Minnesota for High and Low treatments in 2018 were similar, but average High treatment TP was 5.8 times greater than Low in 2019 (Table 2). At Marshfield, average TP concentrations did not differ among control, Low, and Medium; however, High treatment TP was approximately 2-fold greater than Medium.

Concentrations of TS were less variable among treatments compared to DRP or TP (Figures 4–6). Concentrations peaked during the first event in 2018 at Minnesota and decreased for subsequent events, whereas in 2019, concentrations were more stable for melting episodes (Figure 6). Greater TS loss for the Medium treatment at Marshfield occurred until the last two events, when bare soil contributed to large TS losses. While cumulative TS did not differ significantly among treatments, it is interesting to note that at Marshfield, the control had the largest cumulative TS loading. Compared to runoff from bare soils, snowmelt runoff contains fewer total solids and a higher proportion of dissolved nutrient constituents [12,22,39].

Much of the TS load for melting events was likely from manure solids when plots were snow-covered. However, as melting exposed soil, erosion and particle detachment could then contribute TS to runoff. It is possible that the manured treatments at Marshfield helped mitigate soil detachment once soil was exposed sufficiently, as previously mentioned. At Minnesota in 2018, average runoff TS concentrations for High was 2.5 times greater than Low; in 2019, however, average TS did not differ among manure treatments (Table 2).

In a recent winter manure runoff study performed at the Arlington Station, Prasad et al. [25] reported that cumulative losses for DRP and TP were numerically larger for liquid manure (5% solids) compared to semi-solid manure (25.3% to 35.8% solids) and attributed this to the capacity of the more liquid manure to better penetrate the snowpack. Similarly, Komiskey et al. [20] reported large TP and TN load increases when either beef manure or liquid dairy manure was applied within one week of a snowmelt runoff event (compared to fields receiving manure in the fall) but found no significant difference between manure types for N, P, sediment, or runoff losses.

Similar to these studies, our trials indicated that lower solids content manure had some tendency for greater manure solids losses and P mobility with meltwater. Notwithstanding, the High manure solids treatments in our study resulted in equivalent or greater average TP and DRP concentrations compared to the Low and Medium treatments. Mean PUP concentrations/load patterns for manure treatments closely followed TS trends (Supplementary Material Figure S2) and demonstrate the quantitative importance of unreactive P in snowmelt water. Mean PUP concentrations for manure treatments ranged from <0.1 to nearly 12 mg $L^{-1}$. While PUP is not directly bioavailable, desorption of orthophosphate from particulate P or hydrolysis of organic P can contribute to DRP and thus could present more or less of a water quality risk depending on connectivity to overland flow, stream proximity, and site-specific field conditions [40,41].

### *3.5. Snowmelt Runoff Losses of Total Nitrogen, Ammonium, and Organic Nitrogen*

High concentrations of TN and ammonium-N were measured in snowmelt runoff, particularly for the first few melting events (Figures 7 and 8). Mean TN concentration for the High manure solids treatment was >100 mg $L^{-1}$ for the first 2018 Minnesota melting event, with clear and significant separation between treatments. Concentrations dropped rapidly after the first event; however, additional TN spikes for the High treatment were noted later, presumably from melting and transport of manure solids and associated N to meltwater. In contrast, TN for the Low treatment decreased rapidly over the melting period (Figure 7). Peak TN concentrations were noticeably lower in 2019 than 2018 for Minnesota and for Marshfield.

The High treatment at Minnesota (2019) had substantially larger runoff TN with less separation between the control and Low treatment compared to 2018 and more variation in flows that contributed to the lack of treatment differences in 2019 (Figure 7). TN loads were lower for all treatments in 2019 and could be related to the lower manure solids content compared to 2018 (Table 1). At Marshfield, the High and Medium treatments produced similar cumulative TN loads, with large losses for the first few melting events (Figure 7). Overall, TS loss was similar to TN with consistent trends for Low vs. High treatments, suggesting close linkage between TS and TN transport. Manure increased average event TN concentrations by 3.8 to 14.2 times compared to controls (Table 2). The mean High treatment runoff TN concentrations at Minnesota were significantly greater than Low in both years. At Marshfield, mean TN concentrations were greater for the High, with no difference between control, Low, and Medium (Table 2).

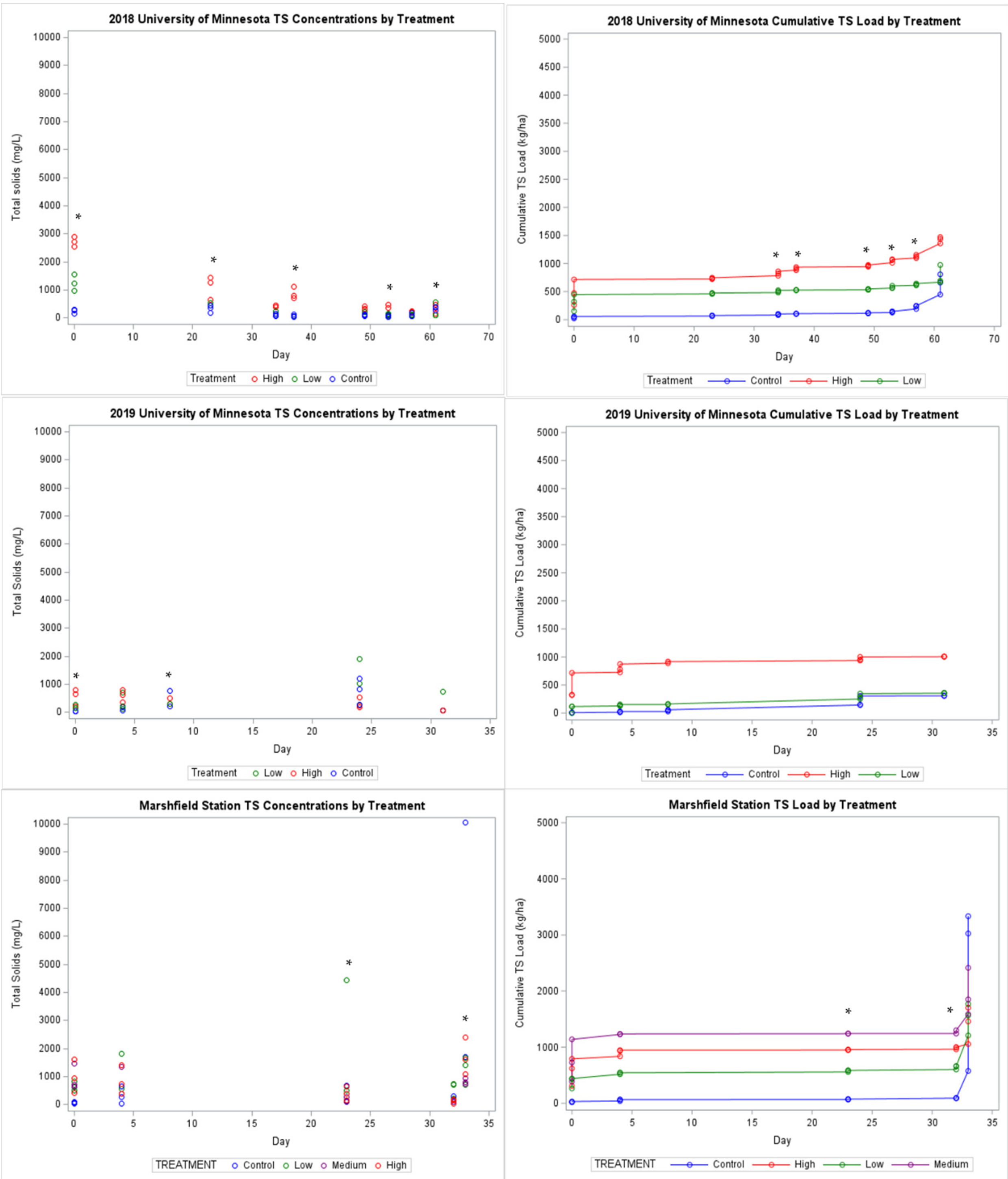


**Figure 6.** Snowmelt runoff total solids (TS) concentrations and loads by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids content.

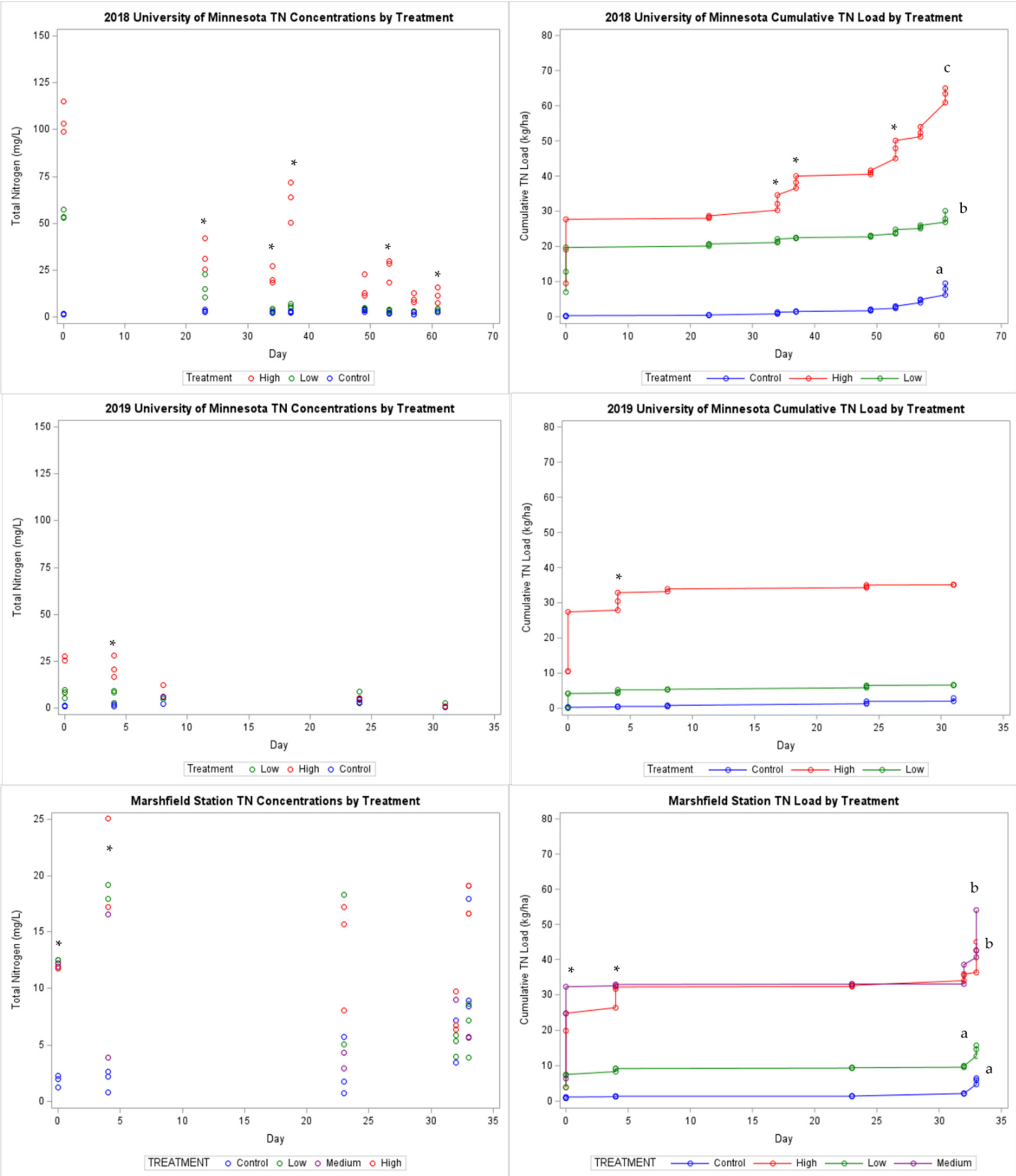


**Figure 7.** Snowmelt runoff total nitrogen (TN) concentrations and loads by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids content. Cumulative loads without a common lower case letter differ ($p \leq 0.05$).

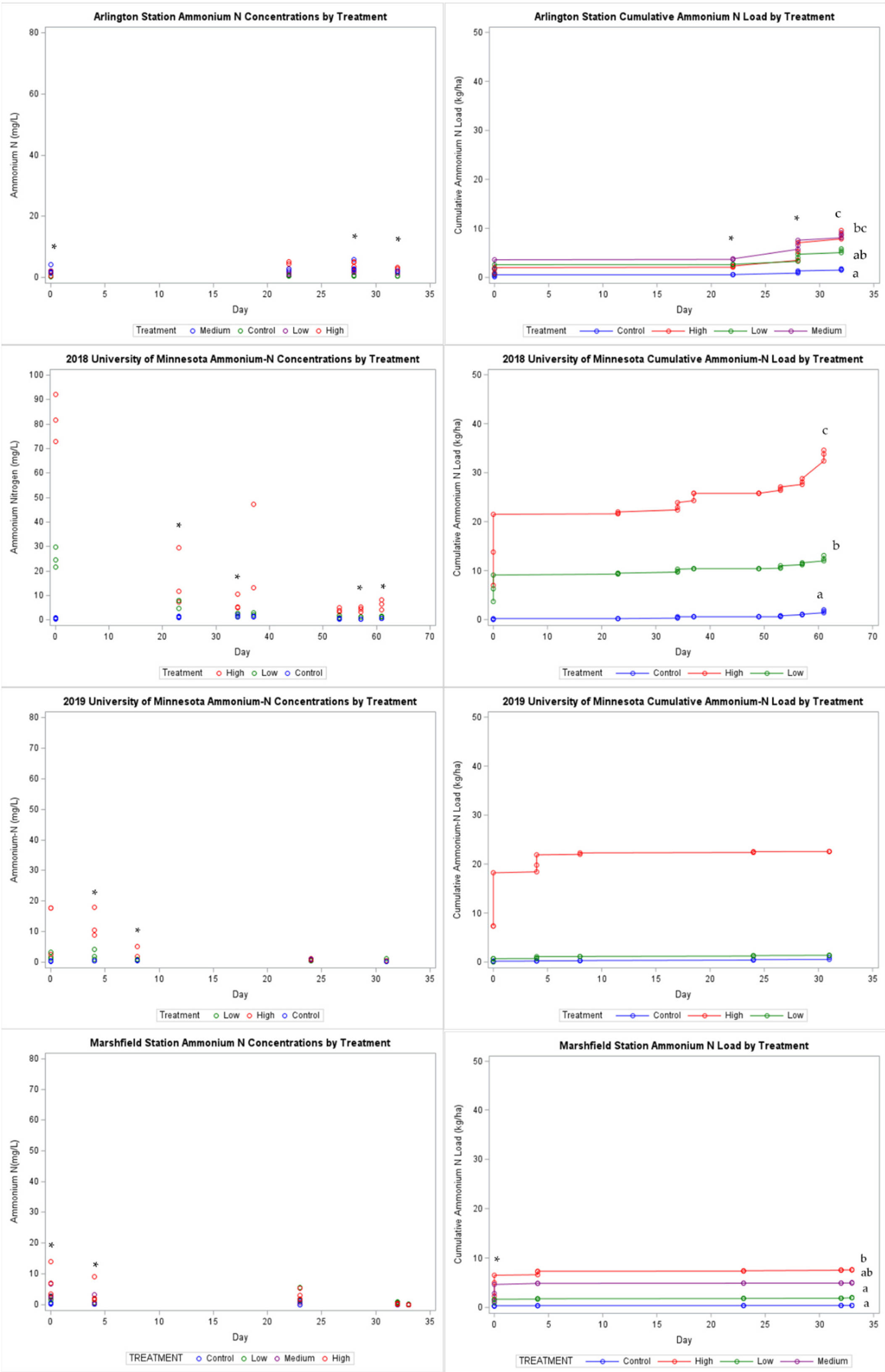


**Figure 8.** Snowmelt runoff ammonium nitrogen concentrations and loads by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids content. Cumulative loads without a common lower case letter differ ($p \leq 0.05$).

Manure treatment ammonium-N concentrations and load trends were generally similar to TN and TS. High and Medium treatments tended to have greater ammonium-N concentrations/loads as anticipated from larger TN applied (Figure 8). In 2018 at Minnesota, ammonium-N concentrations were very high (20 to >90 mg $L^{-1}$) for manure treatments after the first event and much lower in 2019 (Figure 8). In contrast, Arlington had low ammonium-N concentrations and no significant differences among manure treatments; however, the High treatment produced numerically larger cumulative ammonium-N load (Figure 8). Similar to TN results, High had greater ammonium-N concentrations/loads at Marshfield and Minnesota for the few events, with concentrations decreasing thereafter.

While differences in weather and snowpack hydrology were related to ammonium-N losses, manure characteristics may have also played a role. While the Minnesota manure TN content was lower in 2018, solids content was 19.7% compared to 14.6% solids in 2018, contributing to the manure staying more on top of the snowpack rather than infiltrating into the snowpack, potentially increasing interaction frequency between manure solids and meltwater and exacerbating ammonia-N loss [25]. Vadas et al. [19] reported that the placement of liquid manure within the snowpack and the application rate had little effect on ammonium-N lost to snowmelt water under laboratory conditions. For semi-solid manure, ammonium-N concentrations increased with application rate and the depth of snow above, suggesting less volatilization with more snow cover. In our trial, temperatures were below freezing when manure was applied, and much of the ammonium N was presumably dissolved in the liquid fraction and able to penetrate the snowpack. A lack of volatilization may also help explain the very high N concentrations measured in our trial.

A large fraction of TN loss in runoff was organic (Supplementary Material Figure S3). Manure treatment effects on organic-N were similar to TN, TS, and PUP, providing additional support that manure solids constitute an important driver of organic N and P loss in addition to bioavailable forms of N and P. As with PUP, organic-N is not immediately bioavailable; however, it remains an important potential water quality concern since it can be readily mineralized to ammonium-N and further to nitrate-N under appropriate conditions. Moreover, dissolved organic N is readily transported in runoff and is a lost potential source of N for crops. Nitrate-N was also measured but was a very minor component of TN loads (grand mean concentration <1 mg $L^{-1}$ across site-years) and therefore is not discussed here.

### *3.6. Fraction of Applied Nitrogen and Phosphorus Loss as a Function of Manure Solids*

We related cumulative N and P loss in runoff to the proportion of manure solids used in the experiments across site-years (Figure 9). Loss was expressed as mass lost (kg $ha^{-1}$) and as the amount of N and P lost as a fraction of manure-applied N and P (Figure 9). Both N and P losses increased with percent manure solids; however, N and P lost as a fraction of that applied in manure decreased with higher manure solids, suggesting greater transport of lower solids content manure to runoff. Vadas et al. [19] showed that lower solids content manure interacted more thoroughly with the snowpack and was subject to higher runoff losses under laboratory conditions compared to higher solids manure. Prasad et al. [25] reported no significant differences in total N or ammonium-N loads over two years of snowmelt runoff monitoring after liquid and semi-solid manure application at the Arlington Station in south central Wisconsin. Our results similarly indicate that lower solid manures were as vulnerable to transport as the High solids manure and delivered equal or larger N/P loads in some instances and when viewed as a fraction of manure-applied N or P lost in snowmelt runoff (Figure 9).

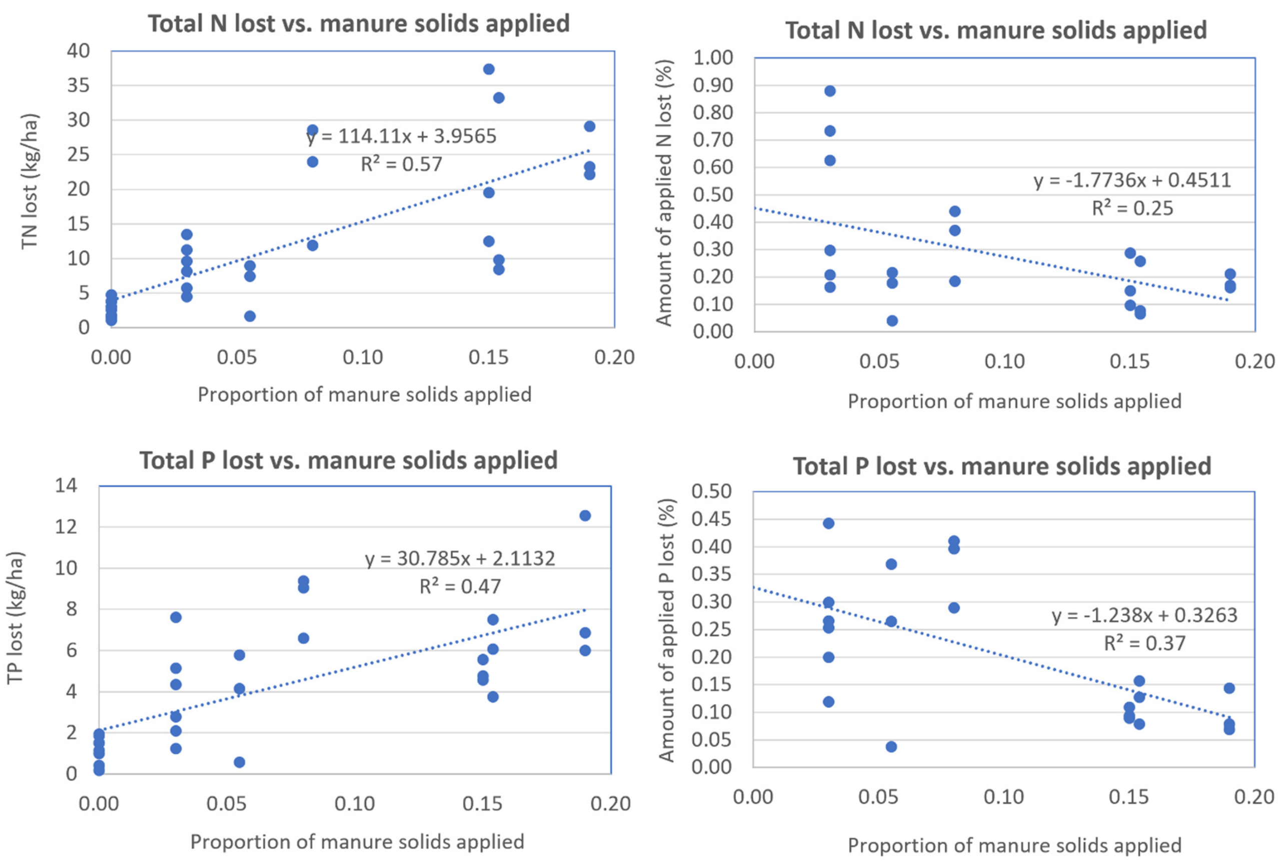


**Figure 9.** Cumulative snowmelt runoff losses of total N (TN) and total P (TP) and the fraction of manure-applied TN and TP lost in runoff as a function of the proportion of manure solids applied across site-years.

### *3.7. Relationships between Phosphorus, Nitrogen, and Total Solids in Snowmelt Runoff*

Our results showed relatively similar patterns among treatments for runoff manure solids, TN, organic-N, TP, and PUP. Given sufficient physical interaction between manure solids and meltwater, there was a clear tendency for larger cumulative TS, TN, and TP loading with the High treatments across site-years, likely driven by the larger amounts of N and P applied (all treatments received equivalent application rates of 26,670 L $ha^{-1}$). An important potential water quality consideration is the average fraction of TP in snowmelt that was orthophosphate and hence bioavailable. There was a strong relationship between TP and DRP concentrations (all site-years included) (Figure 10), with approximately 58% of TP in DRP form (Figure 10). Some other winter runoff studies have reported slightly higher percentages of TP as DRP, attributing this to snow reducing soil erosion and the proportion of particulate P in runoff [22,24]. As expected, snowmelt DRP concentrations were very high for all manure treatments, and while many decreased markedly, they were all well above eutrophication thresholds for TP and DRP. In addition to snowmelt having a higher fraction of dissolved nutrients compared to runoff from bare soils, frozen soils limit infiltration and the surface area available for P sorption, further contributing to greater DRP availability and potential transfer to adjoining surface waters [6].

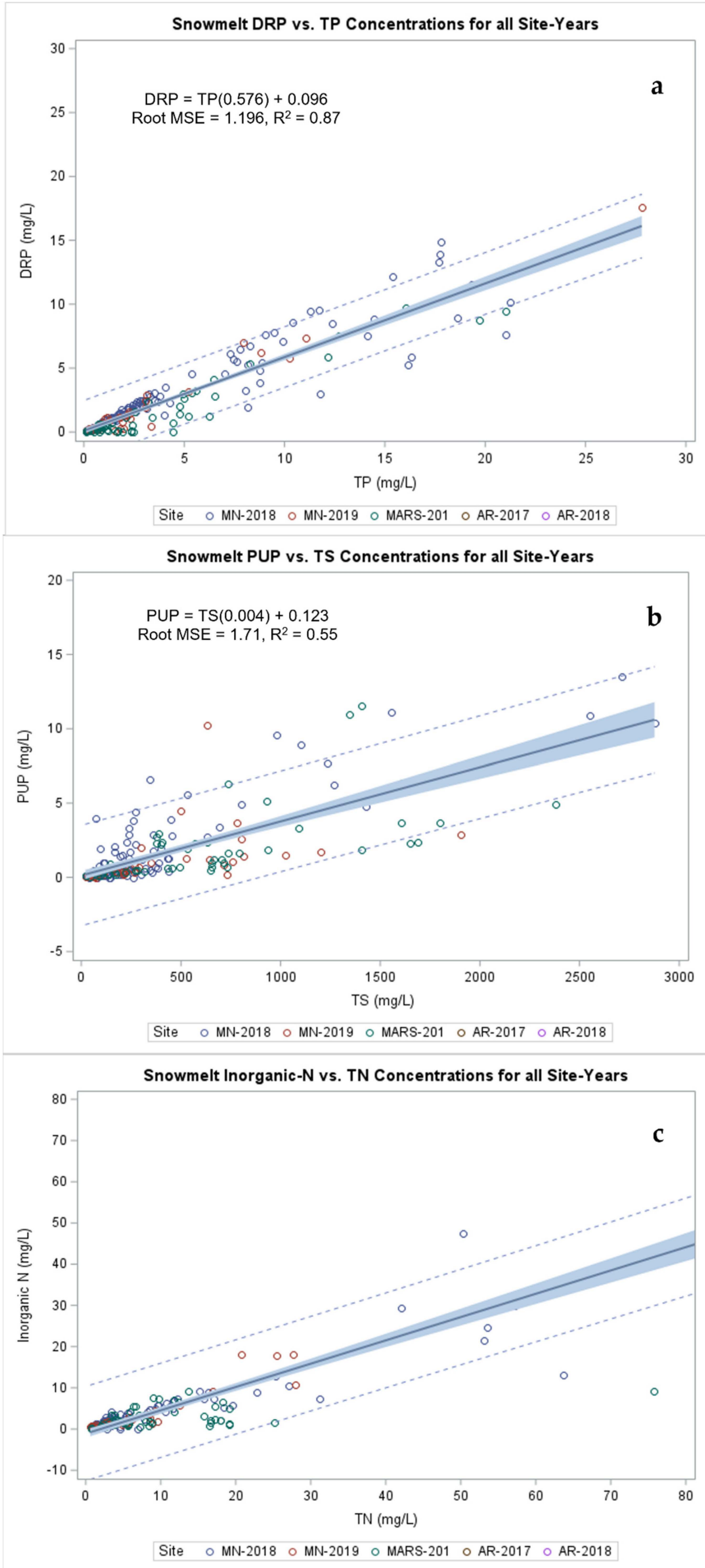


**Figure 10.** Relationships between total phosphorus and dissolved reactive phosphorus (DRP) (**a**), particulate/unreactive P (PUP) and total solids (TS) (**b**), and inorganic and total nitrogen (TN) (**c**), and for all site-years with available data.

Snowmelt PUP and TS concentrations were also linearly related; however, TS was not related to DRP ($R^2$ = 0.05) (Figure 10). Additionally, the ratio of DRP to TP was significantly and negatively related to TS concentrations ($R^2$ = 0.35), further suggesting that PUP was more strongly associated with manure solids. Inorganic-N and TN concentrations were also strongly related, with approximately 57% of TN present as inorganic N and thus bioavailable (Figure 10).

While our main focus was N and P loss from manure application, it is also relevant to consider P loss from controls that did not receive manure. As mentioned, we suspect that soil contributed some P and N to runoff for later events. For the last two events at Marshfield, plots were a mix of bare soil and snow and contributed to elevated solids, N, and P loss. The control at Minnesota in 2018 lost approximately 4 kg $ha^{-1}$ of TP, a relatively high loss considering no manure was applied. Much of the P was likely organic/unreactive, since PUP increased substantially more than DRP. In 2019, less overall TP and DRP were lost from controls, but there was still little difference between Low and control TP loads. At Marshfield, the control had greater mean TP/PUP/TS loads than Low, while the control and Medium had similar mean cumulative TP loading. The results indicate substantial P loss even in control plots, likely related to the high plant-available P concentration. Zopp et al. [24] compiled runoff water quality data for 125 site-years across 26 edge-of-field monitoring studies (Wisconsin and Minnesota) and used regression tree analysis to determine factors controlling dissolved P and TP losses. Manure influenced P losses to a greater extent during frozen than non-frozen periods, and soil test P concentration was the most important determinant of both dissolved and TP loads in frozen conditions, supporting the idea that both manure and soil P contributed to P exported from snowmelt in our trials. At our sites, Bray-1 extractable P was in the high agronomic range for all sites, reflecting legacy P from repeated manure and fertilizer applications and a high desorption potential to runoff compared to soil P levels in the optimum range.

## 4. Conclusions

Our experiments showed that liquid manure application on top of an existing snowpack resulted in high N and P losses in snowmelt runoff and was potentially a high-risk surface water quality condition depending on runoff hydrology and stream proximity. On average, >50% of the TP and TN (concentration basis) was inorganic and bioavailable. Similar to P, manure applied with a higher proportion of solids generally resulted in greater nutrient concentrations/loads of N and P. While N and P tended to decrease with later events, signifying flushing and/or dilution from the snowpack, manure treatments sustained high total and reactive N and P concentrations and loads in meltwater at each event compared to no-manure controls.

While other site factors are important to consider when evaluating P transport risk, field manure management can have a considerable impact on water quality. Finding ways to maximize manure use on growing crops and using fields with low runoff risk for applications when soils are frozen or wet are important considerations with respect to mitigating agricultural nutrient loss and water quality risks. The no-manure controls in our study demonstrated the potential water quality benefits of not applying manure during the winter on top of a snowpack.

Future winter manure research should quantify the range of expected N and P losses based on manure types and other site-specific factors. Due to study design limitations, we were unable to investigate other important hydrologic aspects of winter nutrient loss including snowpack density/water equivalent variation and runoff ratios (runoff/total available water) on runoff timing and losses. Incorporating results from winter manure experiments is important for improving models such as SurPhos and others aimed at predicting daily P loss year-round.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14223745/s1, Figure S1: Daily precipitation (rain and snow) over the study period for each site. There were no precipitation data were available for Arlington in 2017. Figure S2: Snowmelt runoff particulate/unreactive (PUP) by treatment for each site and year of the experiment. Asterisks indicate a significant (p $\leq$ 0.05) main effect of manure solids; Figure S3: Snowmelt runoff organic nitrogen concentrations/loads by treatment for each site and year of the experiment. Asterisks indicate a significant ($p \leq 0.05$) main effect of manure solids content. Cumulative loads without a common lower-case letter differ ($p \leq 0.05$).

**Author Contributions:** Conceptualization, P.V., F.A. and G.F.; methodology P.V., F.A. and G.F.; software, E.Y. and M.W.; formal analysis, E.Y., M.W. and J.S.; investigation, P.V., M.W. and E.Y.; resources, M.W., E.Y. and F.A.; data curation, J.S., M.W., P.V. and E.Y.; writing—original draft preparation, E.Y., J.S. and M.W.; writing—review and editing, E.Y., M.W., J.S. and G.F.; visualization, E.Y., M.W. and J.S.; supervision, P.V. and E.Y.; project administration, E.Y. All authors have read and agreed to the published version of the manuscript.

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