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Persistence and Surface Transport of Urea-Nitrogen: A Rainfall Simulation Study

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Abstract

Studies of harmful algal blooms and associated urea concentrations in the Chesapeake Bay and in coastal areas around the globe strongly suggest that elevated urea concentrations are associated with harmful algal blooms. The observed increased frequency and toxicity of these blooms in recent decades has been correlated with increased agricultural use of N inputs and increased use of urea as a preferred form of commercial N. This rainfall simulation study sought to assess the potential for different N fertilizers and manures to contribute to urea in runoff from a Coastal Plain soil on the Eastern Shore of Maryland. Under worst-case conditions, ~1% of urea-N applied as commercial fertilizer and surface-applied poultry litter was lost in runoff in a simulated rainfall event, roughly equivalent to a 1-yr return period rain storm in the study area, 12 h after application. Cumulative urea-N losses, including four subsequent weekly rainfall events, approached 1.7% from urea-N fertilizer containing a urease inhibitor. Urea-N loss from incorporated poultry litter was negligible, and losses from dairy manure were intermediate. These losses are likely confined to hydrological contributing areas that extend several meters from a drainage ditch or stream for storms with frequent recurrence intervals. Cumulative dissolved N losses in runoff (urea-N + ammonium-N + nitrate-N) as a proportion of total applied plant-available N were <5%, suggesting that most of the applied N was lost by other pathways or was immobilized in soil. Results also highlight the potential for simple management options, such as shallow incorporation or timing, to greatly reduce urea runoff losses.

Core Ideas

- Urea from terrestrial sources can increase frequency and toxicity of algal blooms.
- The proportion of applied urea lost as urea in runoff was quite low (~1%).
- Urea plus urease inhibitors yielded the most urea loss under worst-case conditions.
- Urea "wash-off" soon after application poses the greatest risk to water quality.
- Urea "wash-off" can be mitigated by adjusting method or timing of application.

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Over the past several decades, studies worldwide, nationally, and in the Chesapeake Bay watershed have found that concentrations of inorganic and organic nitrogen (N) have increased concomitantly with the toxicity and frequency of harmful algal blooms in coastal waters (Glibert et al., 2001; Glibert et al., 2006; Heisler et al., 2008; Anderson et al., 2008). Although increases in biologically available N vary regionally, in some areas N fluxes through rivers have increased by 10- to 15-fold in recent decades (Howarth, 2008). It is forecast that N loads from the Susquehanna River to the Chesapeake Bay may increase by up to 17% by 2030 and by up to 65% by 2095 due to the effects of climate change (Howarth et al., 2006). In the United States alone, the annual economic costs of harmful algal blooms in terms of public health, commercial fisheries, recreation and tourism, and monitoring and management are estimated to be in the tens of millions of dollars (Hoagland et al., 2002).

Although many studies in coastal waters have focused on the role of inorganic N in algal bloom development, emerging research suggests that urea ($[NH_2]_2CO$), a key component of the organic N pool, is an equally important causal agent. Urea is of major concern in marine systems because it can support the growth of *Pseudo-nitzschia*, a genus that is present in the Chesapeake Bay (Thessen and Stoecker, 2008; Thessen et al., 2009), particularly during periods of reduced upwelling (Cochlan et al., 2008). Elevated concentrations of urea have been linked to the production of domoic acid by this diatom (Howard et al., 2007; Lelong et al., 2012). Dom++oic acid is a neurotoxin that causes amnesiac shellfish poisoning (Todd, 1993; Watters, 1995). Studies of harmful algal blooms and associated urea concentrations in the Chesapeake Bay (Glibert et al., 2005) and in coastal areas of California (Kudela et al., 2008) strongly suggest that urea is associated with harmful algal blooms.

Increasingly, N from agricultural sources is being considered as a key contributor to harmful algal blooms in coastal waters. Rates of in situ production of urea are too low to sustain the concentrations of urea found in many coastal waters (Lomas et

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Abbreviations: UMES, University of Maryland Eastern Shore.

al., 2002). Although sewage treatment systems have been identified as an external source of urea loads in some coastal systems (Cozzi et al., 2014), the expanded use of urea fertilizer in agriculture has been implicated (Glibert et al., 2014). Specifically, the global increase in toxic blooms corresponds with an increase in total N fertilizer use and a shift away from ammonium nitrate to urea as the dominant form of commercial N fertilizer (Glibert et al., 2006; Glibert et al., 2014). Indeed, urea accounted for about 40% of the total N fertilizer used globally in the mid-1990s (Matthews, 1994) and has increased to 60% currently (Glibert et al., 2014). The amount of urea-N used as fertilizer in agriculture has tripled over the last four decades in certain agricultural regions of the world (Glibert et al., 2006).

It is generally accepted that urea-N applied to soil will be rapidly hydrolyzed to ammonium carbonate by the urease enzyme, after which the N will volatilize to the atmosphere as ammonia or be adsorbed to soil particles as ammonium and subsequently converted to nitrate. Hence, the risk of urea loss in runoff in sufficient quantities to contribute to coastal eutrophication has been perceived as negligible. However, only small concentrations of urea can trigger an algal bloom. Urea-N concentrations >0.09 mg L^{-1} are strong predictors of dinoflagellate blooms in aquaculture ponds (Glibert and Terlizzi, 1999), and urea-N concentrations >0.06 mg N L^{-1} have been correlated with *Pfiesteria* spp. outbreaks in the Chesapeake Bay (Glibert et al., 2004). Because urea in atmospheric precipitation can represent a substantial proportion of the organic N load delivered to coastal waters (e.g., Timperley et al., 1985; Cornell, 2010), only small additions of urea from terrestrial sources are needed to exceed these urea concentration thresholds.

There are several reasons to suspect that direct runoff of urea may be a significant contributor to urea in freshwater systems that are hydrologically connected to coastal waters. First, the rate of hydrolysis to ammonia depends on application rate, soil temperature, moisture, pH, and other factors that influence urease enzyme activity, and complete hydrolysis varies from less than 24 h up to several days (Yadav et al., 1987; Wali et al., 2003; Cartes et al., 2009; Fisher, 2014). Urea is often applied in advance of a predicted light precipitation event to aid hydrolysis and leach N into the topsoil; however, heavy precipitation would result in greater potential for urea washoff in runoff. Second, in many regions, no-till agricultural practices are encouraged to minimize soil erosion. Consequently, surface-applied fertilizers are more likely to leave agricultural fields via overland flow rather than when fertilizers are incorporated into the soil. Third, urease inhibitors are increasingly being added to urea fertilizer to slow the transformation of amide N to ammonium hydroxide and ammonium (Shaviv, 2001; Kiss and Simihăian, 2002; Watts et al., 2014). By slowing this transformation process, N use efficiency is improved, and adverse effects of ammonia production on germination and seedling growth are reduced (Bremner, 1995; Hasan, 2000). However, urease inhibitors can delay the hydrolysis of urea for up to several weeks and thus increase the possibility that runoff will contain urea and not its decomposition products (Prakash et al., 1999).

Although there is extensive information regarding the transport of dissolved ammonium and nitrate from fields to water bodies, significant losses of key forms of dissolved organic N are only recently being recognized in watershed-scale studies (Perakis and Hedin, 2002; Van Breemen et al., 2002). Remarkably few studies have been conducted to measure urea persistence and transport in runoff from agricultural soils. Therefore, this study was designed to determine the persistence and surface transport of urea-N in a coastal plain agricultural soil amended with commercial urea-based fertilizers and animal manures under worst-case conditions of bare soil, high soil moisture, surface application, and relatively steep slope for soils of this area.

Materials and Methods

The topsoil used in the rainfall simulation experiment was collected on the University of Maryland Eastern Shore (UMES) Research and Teaching Farm, a 74-ha tract of agricultural land in Somerset County, MD, near Princess Anne (Fig. 1). The UMES farm is located within the Manokin River Watershed and is approximately 10 km from the Chesapeake Bay. It is characterized by flat topography, with 75% of the farm area possessing slopes less than 3%. Mean annual runoff from the Manokin River (USGS Stream Gauge 01486000) basin was 396 mm from 1981 to 2010, which was approximately 36% of mean annual precipitation (1099 mm) over the same time frame. The 30-yr mean

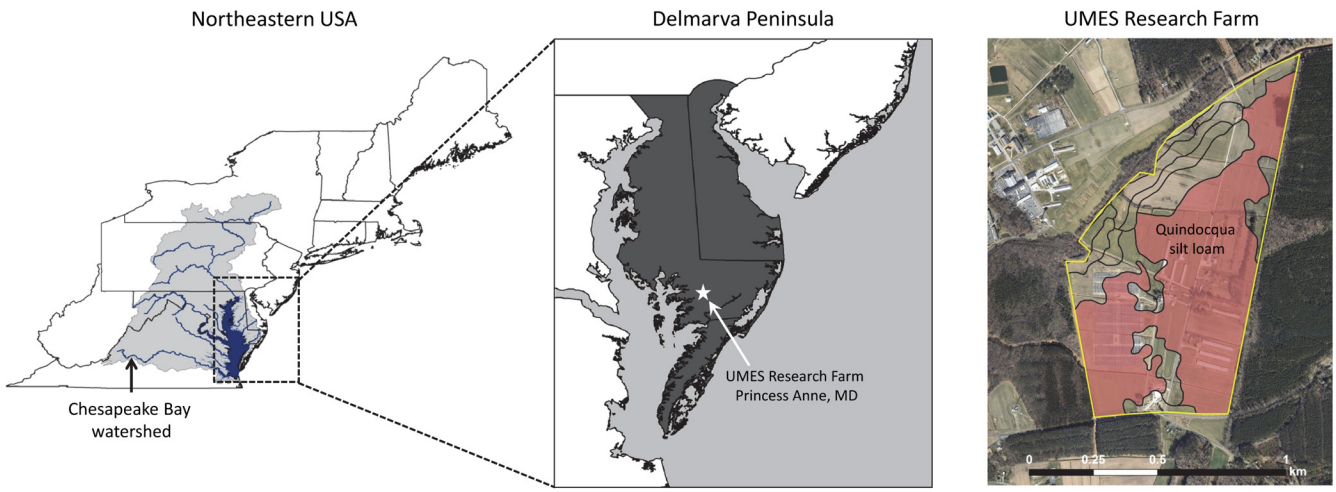

Fig. 1. Site map showing the location of the University of Maryland Eastern Shore (UMES) Research and Teaching Farm on the Delmarva Peninsula and the extent of the Quindocqua silt loam within the farm.

annual temperature was 14.1°C, with mean monthly temperatures ranging from 2.7°C in January to 25.4°C in July (PRISM Climate Group, 2015).

The soil used in this rainfall simulation experiment was a Quindocqua silt loam (fine-loamy, mixed, active, mesic Typic Endoaquult), which is poorly drained and assigned to Hydrologic Soil Group C, indicating a moderately high potential for runoff when wet. Samples of Quindocqua soil (pH 6.0) were collected from the surface horizon of agricultural fields, air dried, thoroughly mixed, and then passed through a 1-cm sieve. Inorganic N was extracted with 2 mol L^{-1} KCl following the method of Mulvaney (1996), with nitrate and ammonium in extracts determined by colorimetry using a flow injection analyzer (Lachat Instruments, 2007, 2008). The ammonium level in the KCl soil extract was below the analytical detection limit (<0.05 mg L^{-1}), and soil nitrate was present at 41.4 mg kg^{-1}.

Two manures were selected to contrast with commercial urea fertilizers. Dairy manure, collected from lactating Friesian dairy cows (*Bos taurus*), was scraped from a free-stall barn at the Penn State dairy facility. Poultry litter was collected from a broiler chicken (*Gallus gallus domesticus*) operation near the UMES Research Farm. The poultry litter and dairy manure used in the study were sent to the Agricultural Analytical Services Lab at Penn State University for analysis. Total N was determined by a combustion method adapted from AOAC 990.03 (Peters et al., 2003). The poultry litter contained 78% dry matter and 38 g total N kg^{-1}. In contrast, the dairy manure contained 22.6% dry matter and 5 g total N kg^{-1}. Plant-available N was calculated following University of Maryland Extension guidelines. Adjustments for mineralization rate and ammonia conservation (tillage practices that reduce volatilization losses) result in plant-available N that is much lower than total N.

Rainfall simulations were conducted in October 2012 following a modified version of the packed-box protocol of the National Phosphorus Research Project as described by Kibet et al. (2014). Stainless steel runoff boxes were 1 m long, 20 cm wide, and 5 cm deep with back walls 2.5 cm higher than the soil surface and had nine 5-mm drainage holes in the base. Cheese cloth was placed on the bottom of each runoff box, and sufficient soil was added to achieve a bulk density of 1.2 g cm^{-3}. The soil surface was bare; no plant residue was added. After packing, the soils were watered to approximate field capacity ($\theta_{fc} \sim 0.30$) and then amended with one of six N fertilizer treatments at a rate of 150 kg plant-available N ha^{-1}. Treatments consisted of an ammonium sulfate prill (included as a nonurea control), incorporated poultry litter, broadcast (surface-applied) poultry litter, dairy manure, urea prill, and a commercially formulated prill containing urea plus a urease inhibitor [N-(n-butyl)-thiophosphoric triamide] and a nitrification inhibitor (dicyandiamide), hereafter referred to as Urea Plus. The prill treatments applied at the established rate resulted in a uniform distribution of prills approximately 1.5 to 2.5 cm apart across the soil surface. Although urea ammonium nitrate solution is sometimes used as a side-dress fertilizer in this area, it was not included in this trial, which was designed to evaluate worst-case conditions for urea loss, because ammonium nitrate solution would likely result in relatively low urea losses in runoff. All amendments were surface applied with the exception of incorporated poultry litter, which was thoroughly mixed with soil before being packed in runoff boxes. Incorporation was included in this trial as a test of this commonly recommended practice for reducing nutrient loss in runoff. Five boxes were prepared for each treatment, resulting in a total of 30 boxes that were subjected to five rainfall events spaced at weekly intervals.

Twelve hours after fertilizer and manure application to the runoff boxes, five weekly rainfall simulation events were administered, with the first one occurring on 3 Oct. 2012. Rainfall simulations were conducted outdoors, and soil boxes were stored under a plastic roof between events. The soil boxes were exposed to ambient light and temperatures during this period, with mean daily maximum temperatures of 22°C and mean daily minimum temperatures of 11°C. The few weeds that sprouted were carefully removed to leave an undisturbed, smooth soil surface. In each event, 2.1 cm of artificial rainfall was applied over 40 min, which was roughly equivalent to a 1-yr return period rain storm in Princess Anne, MD (Bonnin et al., 2006). Between weekly rainfall events, soil moisture was maintained near field capacity by irrigating the soil surface with water using a backpack sprayer to achieve a constant weight for each box. Runoff was generated by applying artificial rainfall on inclined (3%) soil in runoff boxes using a Full jet 3/8HHSS17WSQ nozzle placed approximately 305 cm above the soil surface, as described by Kibet et al. (2014). Rainfall was delivered at a rate of approximately 3.2 cm h^{-1}, with a coefficient of uniformity >0.83 within a 2 × 2 m area directly below the nozzle (as determined on a 20-cm grid spacing). Runoff was routed to 4-L glass bottles via a gutter on the lower edge of the runoff box that was equipped with a canopy to exclude direct input of rainfall. The elapsed time between rainfall and runoff initiation, total duration of the runoff event, and total runoff volume were recorded for each event. At the end of each event, runoff samples were thoroughly mixed and agitated, and two 50-mL subsamples were immediately collected from each glass bottle. Subsamples for urea determination were passed through a 0.7-μm glass-fiber filter, and subsamples for nitrate and ammonium analysis were filtered through a standard 0.45-μm paper filter. All filtered subsamples were stored at 4°C and analyzed within 24 h of collection. The concentrations of urea-N, ammonium-N, and nitrate-N in surface runoff were determined on filtered samples using QuickChem methods 31-206-00-1-A, 10-107-06–2-A, and 10-107-04-1-A, respectively (Lachat Instruments, 2003, 2007, 2008).

Data were analyzed by SAS's PROC UNIVARIATE to confirm assumption of normality and equal variance distribution. Nutrient concentrations (mg L^{-1}) in runoff required logarithmic transformation to achieve normality and were back-transformed for presentation in text and tables. Analysis of variance in PROC GLM (SAS Institute, 2000) and Tukey's honest significant difference test were used to assess treatment differences. Statistical results were considered significant at $p \leq 0.05$.

Results and Discussion

Understanding the hydrologic properties of the artificial rainfall events is critical to interpreting N concentrations and loads in runoff. Mean runoff durations and volumes in the first event were more variable than in the fifth event (Table 1), indicating that successive rainfall simulations served to homogenize the hydrologic characteristics of the packed soil boxes over time and

decrease hydrologic variability. Runoff coefficients, defined as the fraction of simulated rainfall applied that resulted in runoff (not shown), ranged from 0.36 to 0.57 in the first event and then increased to 0.50 to 0.64 in the fifth event, reflecting the more efficient conversion of rainfall to runoff as soil surface conditions became more uniform over the 4-wk study period. Despite the hydrologic variability inherent in earlier runoff events, differences between treatments were influenced more by changes in N concentrations than by fluctuations in runoff volumes, and therefore similar trends were observed when data were analyzed by concentration and load.

Nitrogen Concentrations in Runoff

Urea, ammonium, and nitrate concentrations in runoff are presented in Table 2. For each rainfall event, comparisons were made across treatments for each N form. Letters that show statistical differences are coded by N form (urea, bold; ammonium, italics; nitrate, underlined); comparisons within a column should only be made within the same N form. As expected, concentrations of urea-N in runoff were so great in the first rainfall event that differences between treatments observed in the first event largely carried through to cumulative differences among treatments for the entire experiment (Table 2). The application of Urea Plus and poultry litter to the soil surface yielded significantly higher urea-N concentrations in runoff compared with the other treatments, with the exception of urea prill. Urea-N concentrations in runoff from incorporated poultry litter were not significantly different from the ammonium sulfate control, revealing that mixing a urea source into the soil minimizes or eliminates urea loss in runoff. Urea-N concentrations in runoff from dairy manure were intermediate and significantly lower than concentrations of urea-N from Urea Plus and broadcast poultry litter but significantly higher than concentrations of urea-N in runoff from incorporated poultry litter and the control.

Table 1. Average runoff event durations and runoff volumes recorded for the first and fifth rainfall simulation events.

Treatments	Runoff duration		Runoff volume	
	Event 1	Event 5	Event 1	Event 5
	min		L	
Urea Plus†	25.2 (3.5) ‡	22.4 (1.5)	2.3 (0.5)	2.1 (0.4)
Broadcast litter	24.4 (0.6)	24.0 (1.2)	2.4 (0.1)	2.6 (0.2)
Urea prill	26.6 (0.6)	24.2 (1.3)	1.6 (0.7)	2.4 (0.3)
Dairy manure	24.0 (1.0)	23.6 (0.9)	2.0 (0.2)	2.5 (0.1)
Incorporated litter	23.6 (2.5)	24.6 (0.5)	1.9 (0.7)	2.7 (0.1)
Ammonium sulfate	18.6 (2.4)	24.2 (0.8)	1.5 (0.3)	2.6 (0.1)

† Urea Plus is a commercially formulated prill containing urea plus a urease inhibitor [N-(n-butyl)-thiophosphoric triamide] and a nitrification inhibitor (dicyandiamide).

‡ Values in parentheses are SD.

Table 2. Average N concentrations in runoff over five rainfall simulation events. The first rainfall event was conducted 12 h after treatments were applied; subsequent events were on a weekly basis.

Treatments	N form	Event 1	Event 2	Event 3	Event 4	Event 5
		mg N L^{-1}				
Urea Plus†	urea-N	10.81**a**‡	7.06**a**	2.37**a**	0.15**bc**	0.05**c**
	NH_4–N	1.47*d*	2.57*d*	0.18*cd*	0.13*c*	0.09*cd*
	NO_3–N	0.51c	1.15b	1.96b	1.81c	2.24bc
Broadcast litter	urea-N	6.71**a**	0.77**c**	0.57**c**	0.26**b**	0.13**b**
	NH_4–N	42.02*a*	2.79*cd*	0.22*c*	0.13*c*	2.79*a*
	NO_3–N	4.70a	0.55bc	0.57c	0.65d	0.67d
Urea prill	urea-N	4.63**ab**	0.19**d**	0.09**d**	0.06**cd**	0.06**c**
	NH_4–N	3.48*c*	3.37*c*	0.17*de*	0.11*c*	0.08*d*
	NO_3–N	0.59c	2.25a	6.06a	4.05b	3.37b
Dairy manure	urea-N	1.96**b**	1.44**b**	1.15**b**	0.59**a**	0.46**a**
	NH_4–N	3.76*c*	5.89*c*	0.37*b*	0.23*b*	0.18*c*
	NO_3–N	2.40b	0.52c	0.45c	0.45d	0.88cd
Incorporated litter	urea-N	0.03**c**	0.14**d**	0.03**d**	0.04**d**	0.02**c**
	NH_4–N	0.66*d*	0.66*e*	0.13*e*	0.09*c*	0.08*d*
	NO_3–N	0.52c	0.56bc	0.46c	0.50d	0.62d
Ammonium sulfate	urea-N	0.05**c**	0.13**d**	0.04**d**	0.04**d**	0.04**c**
	NH_4–N	9.33*b*	12.86*a*	0.47*a*	0.40*a*	0.39*b*
	NO_3–N	0.96c	3.21a	4.84a	8.84a	8.18a

† Urea Plus is a commercially formulated prill containing urea plus a urease inhibitor [N-(n-butyl)-thiophosphoric triamide] and a nitrification inhibitor (dicyandiamide).

‡ Values followed by different letters identify groupings per Tukey's honest significant difference test. Letters that show statistical differences are coded by N form (urea, bold; ammonium, italics; nitrate, underlined); comparisons within a column should only be made within the same N form.

Urea-N concentrations in runoff from urea prill were highly variable, with two replicates that closely approximated the mean urea-N concentration in runoff from the Urea Plus treatment (~12.6 mg L^{-1}), two replicates that were much lower in concentration (~1.2 mg L^{-1}), and a fifth replicate that had an intermediate concentration (~5.5 mg L^{-1}). Runoff volume from these urea prill replicates varied from 1 to 2.5 L and showed a strong positive correlation with urea-N concentration (R^2 = 0.94). Previously, Kibet et al. (2014) concluded that urea-N concentration in runoff from surface-applied urea could be explained by comparing the volume of rainfall that infiltrates and leaches urea-N into the soil with the volume of runoff water that transports urea-N over the soil. We attribute the variability observed in urea-N concentrations in runoff from the urea prill treatment to unequal moisture additions to achieve near saturation of the soil surface at initiation of runoff and possible physical disturbance that occurred when the soil boxes were being placed in position under the rainfall simulator. In spite of this variability, it is important to note that under optimum conditions for generating runoff, urea-N concentrations from the urea prill treatment approximate those from the Urea Plus treatment and exceed the mean concentrations of urea-N from the broadcast poultry litter treatment.

Urea-N concentrations from broadcast poultry litter and the urea prill treatments decreased sharply from the first to the second rainfall event, indicating that near-complete hydrolysis of urea had occurred within the 1-wk period between events. In contrast, urea-N concentrations in runoff from the Urea Plus treatment did not fall to background levels until the fourth rainfall event. Clearly, the urease inhibitor slowed the hydrolysis reaction. Although urea-N concentrations in runoff from the dairy manure treatment were initially much lower, they remained above background levels throughout the 4-wk duration of the experiment. The amount of dairy manure applied completely covered the soil surface, such that urea-N near the surface of the manure layer was not in contact with soil that contained the urease enzyme. This physical separation of urea in dairy manure from the soil likely slowed the hydrolysis of urea in the manure, such that urea-N concentrations in runoff above background levels were sustained.

Observed ammonium-N and nitrate-N concentrations in runoff were as expected given the nature of the treatments. Relatively low ammonium-N concentrations were observed in runoff from the Urea Plus treatment in the first two events, and that pulse of ammonium translated to a weak pulse of nitrate in later events. Overall, these concentrations were relatively low to moderate in comparison with other treatments, indicating that the urease inhibitor and the nitrification inhibitor effectively slowed the hydrolysis and nitrification reactions. Elsewhere, in a column leaching study, Sato and Morgan (2008) observed lower N recovery in leachate from a controlled release fertilizer that may have been due to greater N volatilization by these fertilizers. Such an explanation may apply to the relatively weak nitrate pulse observed in the current study.

The highest ammonium-N and nitrate-N concentrations were observed in runoff from the broadcast poultry litter treatment during the first rainfall event, even in comparison to the ammonium sulfate treatment. Nitrogen excreted as uric acid by birds is readily decomposed by one population of aerobic bacteria to form urea, which in turn is hydrolyzed to form ammonia largely by a different population of aerobic bacteria, resulting in an ammonium-rich, alkaline litter (Schefferle, 1965). The highly porous, low-density nature of poultry litter may hold the nutrients above the soil surface when litter is broadcast but not incorporated, minimizing potential interaction between litter N and soil particles and exposing litter constituents to transport in runoff. In contrast, treatments applied in prill form partially dissolved during the 12-h period after treatment application to a near-saturated soil surface and before the first rainfall event, and nutrients had time to adsorb to soil particles or diffuse below the soil surface.

Ammonium-N and nitrate-N in runoff from the urea prill treatment reflect rapid hydrolysis of urea to ammonium and subsequent nitrification to support relatively high nitrate-N concentrations in Runoff Events 3 through 5. Losses of all three forms of N from the dairy manure treatment generally show a decrease over time, suggesting that the original nutrient content is being depleted through successive events, but there is little evidence that hydrolysis and nitrification processes are very active. Incorporation of poultry litter protected against loss of all N forms in runoff over time. The ammonium sulfate treatment supported the highest concentrations of nitrate-N in runoff beginning 1 wk after treatment application, reflecting the rapid onset of the nitrification process.

Nitrogen Loads in Runoff

Urea, ammonium, and nitrate loads in runoff are presented in Table 3. As in Table 2, for each rainfall event, letters that show statistical differences across treatments for each N form are coded by N form (urea, bold; ammonium, italics; nitrate, underlined); comparisons within a column should only be made within the same N form. In comparing Table 3 and Table 2, differences in loads across treatments and within individual runoff events as indicated by letters identifying grouping per Tukey's honest significant difference test are strikingly similar to differences in concentration in spite of the fact that volume of runoff was variable to a greater or lesser degree depending on treatment. This can be explained by the previously discussed positive correlation between concentration and runoff volume observed in runoff event one for urea prill. This relationship is more or less discernible across all treatments to a greater or lesser degree, so the net effect is amplified when urea-N loads were evaluated (Table 3).

Loads for each N form were summed to produce graphics depicting cumulative N loads in runoff over the 4-wk duration of the experiment (Fig. 2). The total cumulative load of urea-N (50 mg) in runoff from the Urea Plus treatment was more than double the load in runoff from broadcast poultry litter (Fig. 2). It should be reiterated that under the conditions of this experiment, whereby initially saturated treated soils were kept at near field capacity by daily light applications of water sprayed onto the surface, urea-N losses during later events represent a worst-case scenario. Dawar et al. (2011) demonstrated that when urea fertilizer combined with a urease inhibitor was applied to a silt loam soil at 50% of field capacity, subsequent surface irrigation caused urea to move away from the surface to the subsurface soil layer where it would not be as susceptible to loss in runoff. Although the mean load of urea-N in runoff from urea prill during Runoff Event 1 (14 mg) was similar to broadcast poultry litter, two of

Table 3. Average N loads in runoff over five rainfall simulation events. The first rainfall event was conducted 12 h after treatments were applied; subsequent rainfall events were on a weekly basis.

Treatments	N form	Event 1	Event 2	Event 3	Event 4	Event 5
		mg N				
Urea Plus†	urea-N	23.9**a**‡	16.6**a**	6.3**a**	0.3**c**	0.1**c**
	NH_4–N	3.3*cd*	6.0*d*	0.5*b*	0.3*c*	0.2*c*
	NO_3–N	1.1c	2.7c	5.2b	3.8c	4.7bc
Broadcast litter	urea-N	15.7**a**	2.1**c**	1.3**c**	0.6**b**	0.3**b**
	NH_4–N	98.7*a*	7.5*cd*	0.5*b*	0.3*c*	5.2*a*
	NO_3–N	11.0a	1.5d	1.3c	1.4d	1.4d
Urea prill	urea-N	7.2**ab**	0.5**d**	0.2**d**	0.1**cd**	0.1**bc**
	NH_4–N	5.3*bc*	8.5*c*	0.4*b*	0.2*c*	0.2*c*
	NO_3–N	0.9c	5.6b	14.6a	8.6b	8.0b
Dairy manure	urea-N	3.8**b**	3.8**b**	3.0**b**	1.4**a**	1.1**a**
	NH_4–N	7.2*bc*	15.6*b*	1.0*a*	0.5*b*	0.4*bc*
	NO_3–N	4.7b	1.4d	1.2c	1.1d	2.2cd
Incorporated litter	urea-N	0.1**c**	0.4**d**	0.1**d**	0.1**d**	0.1**c**
	NH_4–N	1.3*d*	1.8*e*	0.3*c*	0.2*c*	0.2*c*
	NO_3–N	1.0c	1.5d	1.1c	1.1d	1.6cd
Ammonium sulfate	urea-N	0.1**c**	0.4**d**	0.1**d**	0.1**d**	0.1**c**
	NH_4–N	13.7*b*	34.7*a*	1.0*a*	0.8*a*	1.0*b*
	NO_3–N	1.4c	8.7a	10.0a	18.5a	21.0a

† Urea Plus is a commercially formulated prill containing urea plus a urease inhibitor [N-(n-butyl)-thiophosphoric triamide] and a nitrification inhibitor (dicyandiamide).

‡ Values followed by different letters identify groupings per Tukey's honest significant difference test. Letters that show statistical differences are coded by N form (urea, bold; ammonium, italics; nitrate, underlined); comparisons within a column should only be made within the same N form.

the replicates produced urea-N loads in runoff (~29 mg urea-N) that were comparable to loads from the Urea Plus treatment. However, the additional urea-N in runoff from urea prill during subsequent events was negligible. Initial urea-N loads in runoff from the dairy manure treatment were low but were persistent in subsequent events such that the cumulative load in runoff (13 mg urea-N) was comparable to the load from urea prill.

Cumulative loads of urea-N + ammonium-N + nitrate-N (U+A+N) were greatest in runoff from the broadcast poultry litter treatment (150 mg N), due primarily to the loss of ammonium-N in the first event. The second highest cumulative load of U+A+N was in runoff from the ammonium sulfate treatment (113 mg N) occurring equally as ammonium and nitrate. However, ammonium-N loads had leveled off during later events as nitrate-N loads continued to climb. If the experiment had been continued for another week, U+A+N loads from the ammonium sulfate treatment may have equaled that from the broadcast poultry litter treatment.

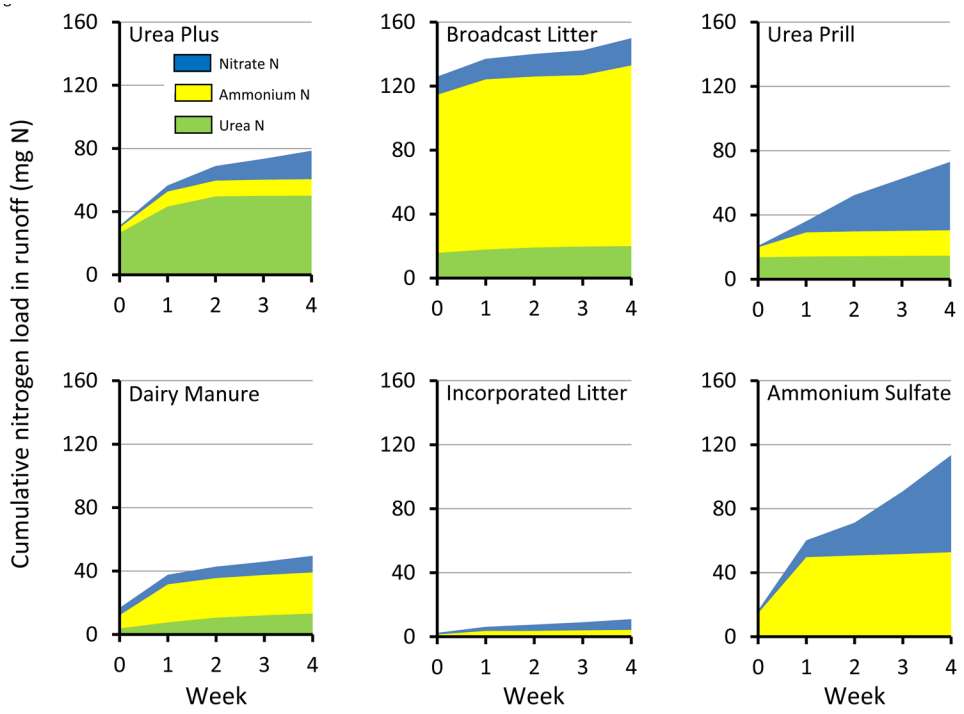

Fig. 2. Cumulative losses of urea-N, ammonium-N, and nitrate-N in runoff over the 4-wk duration of the experiment (five runoff events). Urea Plus is a commercially formulated prill containing urea plus a urease inhibitor [N-(n-butyl)-thiophosphoric triamide] and a nitrification inhibitor (dicyandiamide).

The U+A+N loads in runoff from the urea prill treatment and the Urea Plus treatment were approximately the same (~75 mg), but differences in N form reflect the effects of the urease inhibitor and the nitrification inhibitor in Urea Plus. The U+A+N load in runoff from the urea prill treatment after the second event averaged 36 mg, approximately half the amount of U+A+N load in runoff from the ammonium sulfate treatment (60 mg) at the same time (1 wk after fertilizer application). These results are comparable to those in a study by Moe et al. (1968), who reported mineral N loads in runoff from ammonium nitrate–amended soils that were approximately double that from urea-amended soils. Total nitrate-N loads in runoff from the ammonium sulfate treatment averaged 60 mg, compared with 45 mg from the urea prill treatment. In a soil incubation study, Gandhi and Paliwal (1976) observed lower pH, greater net mineralization, and greater net accumulation of nitrate in an ammonium sulfate–amended soil than in a urea-amended soil, attributing the difference to less ammonia volatilization under more acidic conditions.

Cumulative loads of U+A+N in runoff from the dairy manure treatment were the lowest among the treatments in which N sources were surface applied. This largely reflects the losses of N that occur from a manure-covered surface, such as a feedlot. Although dairy manure contains large quantities of N, only the surface of the manure layer is exposed to N loss in runoff. As shown by the results from the incorporated poultry litter treatment, mixing of a N source into the soil is an effective way to minimize N losses in surface runoff. Technologies exist for incorporating (or injecting under no-till conditions) all of these N treatments, although poultry litter injection is still in the development stage (Pote et al., 2011).

Perspectives on the Risk of Urea-Nitrogen Losses to Surface Waters

Punctuated deliveries of urea-N to runoff immediately after the application of fertilizer or manure represent the greatest risk to water quality in the short term. Indeed, urea-N concentrations in runoff from soils receiving surface amendments of fertilizer (urea plus and urea prill) and manure (poultry litter and dairy manure) were highest in the first rainfall event occurring 12 h after application (Table 2). This pattern highlights the importance of incidental urea-N transfers, or fertilizer "wash-off" processes, that are readily observed in studies of phosphorus runoff (Preedy et al., 2001; Withers et al., 2003). Notably, broadcasting urea fertilizers, such as Urea Plus and urea prill, to saturated soils immediately before the first rainfall event yielded urea-N concentrations in runoff that were 51 to 120 times greater than the urea-N concentration threshold for harmful algal bloom development in coastal waters (~0.09 mg L^{-1}) (Glibert et al., 2004). However, these results represent worst-case conditions in a study that is a poor representation of actual field conditions. Although elevated urea-N concentration spikes represent a concern to water quality protection, they are largely ephemeral in nature and could be mitigated by adjusting the timing of urea fertilizer application to avoid conditions (high soil moisture, impending heavy rainfall) that promote fertilizer "wash-off." Implementing this management strategy would be most critical in the springtime (March–May) when urea fertilizers and livestock manures are most commonly applied to fields before planting.

Even though concentrations of urea-N in runoff were elevated, especially in the first rain event, the proportion of applied urea-N lost as urea-N in runoff was quite low (Table 4). For Urea Plus and urea prill, in which all N was assumed to be in the form of urea, up to 0.88% of applied urea-N was lost as urea-N in the first runoff event, with cumulative urea-N losses approaching 1.67% of what was applied after four successive rainfall events had occurred. Perhaps more important was the fact that cumulative dissolved N losses in runoff (urea-N + ammonium-N + nitrate-N) as a proportion of total plant-available applied N were less than 5% (Table 4), suggesting that most of the applied N was lost by other pathways or was immobilized in soil.

Even when all N forms are considered, the fraction of applied N lost in runoff in this study is much less than what is reported elsewhere in the literature. In their review of the links between increasing urea fertilizer usage and coastal eutrophication, Glibert et al. (2006) suggested that surface-applied urea-N losses in runoff could range from 3 to 5%. A much earlier study by Dunigan et al. (1976) pointed to the potential for up to 6.8% of applied urea-N to be lost as urea-N in runoff, but these losses occurred after a 10-cm rainfall event with a return period of at least 2 to 5 yr. Empirical data reported herein suggest that much lower fractions of fertilizer urea-N are transferred to runoff (Table 4) during more routine rain storms (1-yr return period), even when conditions supporting efficient runoff generation (wet soils, moderate-to-heavy rainfall intensity) are maintained during successive events (Table 1).

Table 4. Urea-N and dissolved N loads for the first rainfall event and summed across all five events.

Treatments	Urea-N load		Dissolved N load†	
	Event 1	Cumulative	Event 1	Cumulative
	mg (% N recovered)			
Urea Plus‡	26.5 (0.9)	50.1 (1.7)	31.0 (1.0)	78.6 (2.6)
Broadcast litter	15.8§	20.0	125.9 (4.2)	149.9 (5.0)
Urea prill	13.7 (0.5)	14.6 (0.5)	20.8 (0.7)	73.0 (2.4)
Dairy manure	3.8	13.2	16.8 (0.6)	49.6 (1.7)
Incorporated litter	0.1	0.7	2.5 (0.1)	11.0 (0.4)
Ammonium sulfate	0.1	0.7	16.5 (0.6)	113.4 (3.8)

† Dissolved N loads (urea-N + nitrate N + ammonium N) are reported relative to the total amount of applied plant-available N (3000 mg) per box.

‡ Urea Plus is a commercially formulated prill containing urea plus a urease inhibitor [N-(n-butyl)-thiophosphoric triamide] and a nitrification inhibitor (dicyandiamide).

§ Initial urea-N applied to soil was not measured and percent urea-N recovered in runoff could not be estimated.

Although the use of packed soil boxes provides insight into the effects of applied fertilizer and manure sources on urea-N in runoff, their homogeneous nature limits the transferability of the findings to diverse agricultural landscapes (Srinivasan et al., 2007). For instance, maintaining constant wet conditions in runoff boxes assures that urea-N sources are readily connected with surface waters (i.e., the outlet of the box) by the efficient contribution of runoff from the entire area of the box. In the flat agricultural landscapes characteristic of the Atlantic Coastal Plain, hydrological contributing areas (i.e., areas that are hydrologically connected to surface waters) are likely confined to zones that extend several meters from a drainage ditch or stream for storms with frequent recurrence intervals. Recent studies using conservative tracers in tile-drained landscapes support this statement, showing that the annual capture zone for nutrients reaching tile drainage is very close to the tile itself, sometimes within 4 m or less on either side of the tile (Frey et al., 2012). Moreover, work by Kleinman et al. (2007) on the UMES Research Farm demonstrated that overland flow adjacent to field ditches accounted for only 8% of ditch drainage water, further supporting the assertion that surface contributing areas are likely proximal to ditches and streams. Findings from this study should therefore be interpreted as a worst-case scenario in which fertilizer and manure sources of urea-N are applied in hydrologically active areas that are close to ditches and streams. Further research is needed using larger runoff plots under natural and artificial rainfall conditions to better understand how the risk of urea-N transfers in runoff relate to factors such as the rate and timing of nutrient application, the frequency and timing of rainfall events, the rate and connectivity of hydrological processes, and the effectiveness of setback areas where no nutrients are applied within a fixed distance of a water body, stream, or drainage ditch.

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