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STREAM CHEMISTRY AFTER AN OPERATIONAL FERTILIZER APPLICATION IN THE OUACHITA MOUNTAINS[1]

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Abstract—The amount of forested land annually fertilized in the southern United States has increased rapidly in the past 10 years. Although forest growth responses to fertilizer are fairly well understood, knowledge concerning the effects of fertilization on stream chemistry and health in this region is limited. To better understand the potential changes in stream chemistry after operational forest fertilization in the Ouachita Mountains of Arkansas, levels of N were monitored in a stream after application of 437 kg ha^{-1} of urea and 140 kg ha^{-1} of diammonium-phosphate to a 150 ha watershed. Baseflow and stormflow concentrations of NO_3^--N, NH_3-N, and Total Kjeldahl N were measured at the outlet of the fertilized subwatershed, the outlet of a reference subwatershed, and downstream of both in the main watershed prior and up to three months after fertilization application. Maximum NO_3^--N and NH_3-N concentrations prior to fertilization were respectively 0.3 and <0.01 mg L^{-1}. Nitrate-N concentrations peaked at 3.58 mg L^{-1} during a storm event 50 days after urea application while NH_3-N levels peaked at 4.91 mg L^{-1} 24 hours after urea fertilization. Concentrations of total organic nitrogen (Total Kjeldahl N – NH_3-N) peaked at 44.5 mg L^{-1} five hours after urea application. Nitrate-N concentrations remained elevated for 78 days after urea fertilization. The unexpectedly rapid increase and high levels of N after application appear to be related to an extremely large precipitation event which occurred within 24 hours of fertilizer application and to direct application of fertilizer to intermittent and ephemeral stream channels.

INTRODUCTION

In the past 10 years the use of fertilizer to increase productivity of southern pine forests has increased dramatically. The reported area of fertilized loblolly has increased from approximately 128,000 acres in 1988 to 890,000 acres in 1997 (North Carolina State 1998). Although there has been a rapid growth in fertilizer use, information documenting the potential changes in stream chemistry resulting from forest fertilization in the southern United States is minimal. The available research, much of it from the 1970's, indicates that application of fertilizer typically causes a short-lived peak in several constituents followed by low-level alterations in stream chemistry for two to three years after application. Aubertin and others (1973) documented a sevenfold increase in average NO_3^--N concentrations during the first 9 months and an 18 percent increase in total N discharged in the first year following application of 225 kg ha^{-1} of urea to a West Virginia watershed dominated by second growth hardwood. Patric and Smith (1978) reported that in this same watershed NO_3^--N and Ca^{2+} concentrations were significantly elevated above pre-fertilization concentrations for respectively, two and three years after fertilization application. Helvey and others (1989) reported similar changes in stream chemistry after application of 336 kg ha^{-1} N as ammonia nitrate and 224 kg ha^{-1} P_2O_5 in another pair of watersheds dominated by second growth hardwoods located in this same area of Western Virginia. Stream water concentrations of NO_3^--N rapidly increased and at times were above drinking water standards but concentrations of P were unaltered (Helvey and others 1989). Nitrate-N concentrations after this fertilizer application were still higher in the treatment than control watersheds nine to ten years after the application. Edwards and others (1991) reported that the outputs of NO_3^--N, Ca^{2+}, and Mg^{2+} from these treated watersheds were significantly greater than predicted by control watersheds for the first three years after application.

These studies generally demonstrated that while urea-N and NH_3-N concentrations rise immediately after fertilization and quickly return to pre-fertilization levels, NO_3^--N levels remain elevated for extended periods of time after fertilization. Peak concentrations of ionic N occur during stormflow events and storm characteristics such as size and intensity influence peak concentrations to a greater degree than absolute fertilization rates. However, cumulative effects of fertilization, both temporally and spatially, have not been considered.

Forest fertilization in the Ouachita Mountains of Arkansas primarily occurs in watersheds dominated by loblolly (*Pinus taeda* L.) and shortleaf pine (*Pinus enchinata* Mill.). Streams in this region supply much of the drinking water for local urban centers and are valued for their recreational use. To better understand the potential effects of operational fertilization on these streams, water chemistry was monitored during and after an operational fertilization of a 150 ha watershed in the Ouachita Mountains. The objectives of the study were: 1) to quantify changes in NO_3^--N, NH_3-N, and Total N concentrations in the fertilized watershed 2) to determine the duration of the changes in N concentrations, 3) evaluate whether these changes in N chemistry persists downstream from the area of fertilizer application, and 4) gather information for further fertilization and analysis of cumulative effects.

METHODS

Study Site

Research was done in the Little Glazypeau watershed located approximately 20 km from Hot Springs, Arkansas (fig. 1). The watershed encompasses 2,273 ha, has an elevation between 209-381 m, has a southwest aspect, and contains 33 km of perennial streams. Approximately 50 percent of the watershed contains loblolly pine plantations while the remaining 50 percent of the watershed contains mixed pine-hardwood stands, natural short-leaf pine stands,

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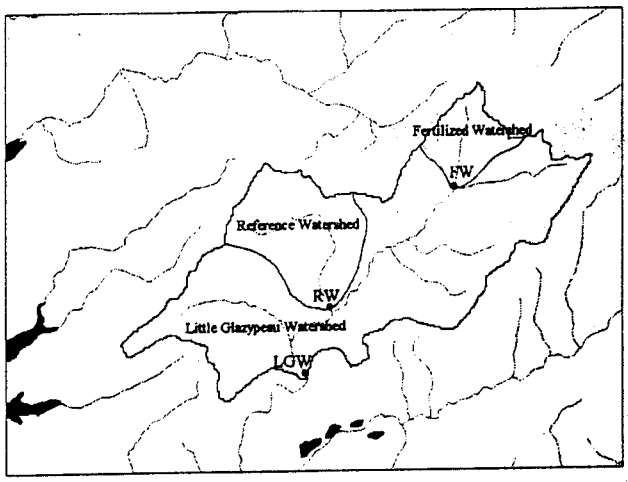

Figure 1—Study watersheds and outlet monitoring stations.

cleared land, or land dominated by shrubs and brush. Two subwatersheds as well as the outlet of the basin were the focus of the study. The subwatershed that was fertilized (FW) is 150 ha in size (fig. 1). Loblolly pine plantations occupy 138 ha while mixed hardwood-pine stands occupy 12 ha of the FW. The second subwatershed which is 325 ha in size was used as a reference (RW). The RW contains 104 ha of pine plantations. Mixed hardwoods, natural pine stands, and shrub/bush vegetation dominates the remaining 221 ha. The 150 ha basin had not been previously fertilized, but a 76 ha pine plantation in the reference basin had been fertilized the year before the study. Stream water was monitored at the outlets of the FW, RW, and larger Little Glazypeau watershed (LGW). The monitoring station in the LGW is approximately 6.5 km below the FW station.

Fertilizer Application

A total of 437 kg ha^{-1} urea was applied to the FW on February 9, 1998 and another 140 kg ha^{-1} of diammonium phosphate (DAP) was applied 77 days later. Delivery of N was 201 kg ha^{-1} and 25 kg ha^{-1} from the urea and DAP applications respectively. Application of the fertilizer was by helicopter using a bucket spreader. It took four hours to apply the urea and two hours to apply the DAP. Perennial stream channels and streamside management zones surrounding these stream channels were avoided during application. However, non-perennial channels and the associated surrounding riparian areas did receive the same fertilizer application as the upland portions of the watershed.

Sample Collection and Stream Measurements

Stream stage and velocity were measured every 10 minutes at each of the three outlets, with data collection beginning in the summer of 1996 at the FW and LGW outlets and shortly before fertilization in the RW. Stream stage and velocity was monitored using Starflow Ultrasonic Doppler #6526 Instruments. Stream stage was also measured in stilling wells using Belfort water level recorders equipped with FW1 potentiometers. Precipitation was measured using tipping rain gages at each station and stream water samples were collected using ISCO 3700 pump samplers. A Campbell CR10X Data logger recorded potentiometer stage as well as precipitation amounts, and used the stage measurement to initiate and control timing of the water sample collections by the ISCO 3700 samplers beginning in December of 1997. Historical stage data was used to design a unique sampling scheme for each outlet. A critical stage measurement initiated hourly storm event sampling and a critical increase in stage between successive 10-minute stage measurements was used to collect additional samples during rapid increases in discharge. Baseflow sampling ranged from hourly to weekly with the most intensive sampling occurring just prior to, during, and shortly after fertilization application.

Sample Analysis

Nitrate-N and NH_3-N concentrations were determined for every water sample but to reduce analysis costs Total Kjeldahl N (TKN) concentrations were only determined for every other water sample. Since N measured as TKN includes NH_3-N, urea-N, and other forms of organic N, total organic N (TON) was computed by subtracting NH_3-N from TKN. Nitrate-N concentrations were determined using ion chromatography. Ammonia-N concentrations were determined colormetrically using a Latchat 2000 flow injection system. TKN was determined in the same manner after digestion with sulfuric acid. All concentrations were determined after filtration with 2.0 µm filter paper. To calculate mean concentrations over a given time period, concentration below detection limits (<0.01 mg L^{-1}) were given a value of 0.005 mg L^{-1}. All mean concentrations were calculated from concentrations unadjusted for discharges.

RESULTS AND DISCUSSION

Precipitation During the Study

A total of six storm events were sampled prior to fertilization. Average recorded precipitation amounts for these events at the LGW outlet was 8.19 cm (3.23 in). Within 10-12 hours after urea application, a storm event began that produced 29.0 cm (11.43 in) of precipitation during a 26-hour period at the maximum point recorded in the watershed. At the outlet, the rainfall measured 24.6 cm (9.68 in). The maximum point 24-hour rainfall was 10.64 inches, well above the 100-year, 24-hour rainfall of around 9 inches (USDA Dept. of Commerce, 1961). Stream stage at the RW outlet increased from 0.21 to 3.54 feet in less than eight hours. This no doubt represents a potential worst-case scenario for fertilizer movement due to overland and channelized flow. Another seven precipitation events occurred after the February 10th event before the end of the study on April 9.

Urea Application

Only 17 to 19 percent of the samples collected prior to fertilization application had detectable NH_3-N concentrations (<0.01 mg L^{-1}). Mean NH_3-N concentrations prior to fertilization were below detection limits at all outlets as well (table 1). TON concentrations were generally between 0.5 and 0.8 mg L^{-1} prior to fertilization. No discernable difference in TON concentrations were evident among stations in pre-fertilized stream samples shown in Table 1. However, prior to fertilization NO_3^--N concentrations were consistently greater at the RW outlet than at FW or LGW outlets. Mean pre-fertilization concentration at the RW outlet was approximately 0.19 mg L^{-1} and 0.26 mg L^{-1} greater than NO_3^--N concentrations at the LGW and FW outlets, respectively (table 1). Differences in pre-fertilization NO_3^--N may reflect prior fertilization application in the reference subwatershed or differences in vegetation and soils within the Little Glazypeau watershed.

Table 1—Mean (standard deviations in parenthesis) N concentrations (mg L^{-1}) and number of samples (n) of stream water prior to urea fertilization (12/7/1997-1/26/98) and prior to DAP fertilization (3/31/98-4/26/98) at each watershed outlet

	NH_3-N		NO_3^--N		TON	
Watershed	Mean	n	Mean	n	Mean	n
			Pre-urea fertilization (mg L^{-1})			
FW	<0.01(<0.01)	82	0.03(0.04)	105	0.47(0.12)	53
RW	<0.01(<0.01)	90	0.29(0.05)	108	0.43(0.09)	54
LGW	<0.01(<0.01)	114	0.10(0.03)	142	0.46(0.14)	71
			Pre-DAP fertilization (mg L^{-1})			
FW	<0.01(<0.01)	38	2.22(0.96)	40	0.46(0.14)	20
RW	<0.01(<0.01)	26	0.14(0.01)	26	0.34(0.11)	12
LGW	<0.01(<0.01)	14	0.24(0.16)	14	0.31(0.18)	8

Concentrations of TON dramatically increased after urea fertilization (fig. 2). TON concentrations increased from approximately 0.3 mg L^{-1} to 44.5 mg L^{-1}, its maximum level, five hours after completing urea application. The dominant N constituent measured as TON during this time period was undoubtedly urea-N. As the urea began to hydrolyze, levels of NH_3-N also rapidly increased in the fertilized subwatershed. However, the highest concentration of NH_3-N measured within the first 11 hours after urea application and prior to a storm event was only 1.5 mg L^{-1}. Due to the microbial mediated mechanisms involved with the conversion of NH_3 to NO_3^-, NO_3^--N concentrations also increased but more slowly than TON or NH_3-N (fig. 2).

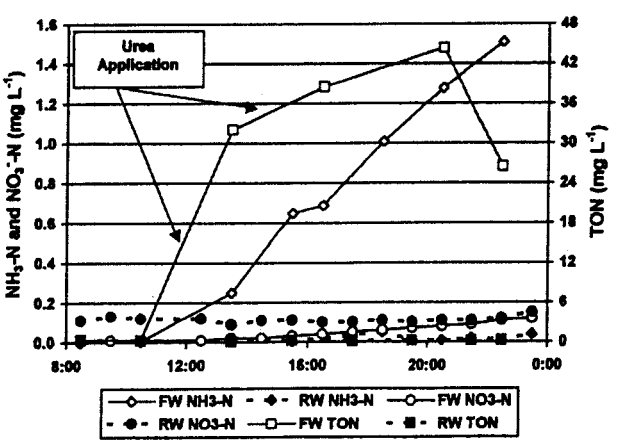

Figure 2—NH_3-N, NO_3-N, and TON concentrations prior and within 12 hours of initiation of urea application at the outlets of the fertilized (FW) and reference (RW) subwatersheds.

The cold temperatures during this period may have contributed to the slow microbial conversion of NH_3. Assuming that the majority of the TON is urea-N, transient levels found in the FW outlet are much higher than urea-N levels observed in six fertilization studies from northwestern United States summarized by Fredriksen and others (1975). However, Bisson (1982) measured a short-lived Total-N peak of 37.5 mg L^{-1} after application of 224 kg ha^{-1} urea to a watershed located in the state of Washington. This high level of N was attributed the direct application of the urea to the stream and snow covered soil, both practices currently avoided. As in this study, the peak occurred the day of fertilization, immediately dropped, and was down to 1.5 mg L^{-1} 72 hours later.

TON concentrations decreased from a maximum of 44.5 mg L^{-1} to 11.6 mg L^{-1} 21 hours after application. Concentrations continued to decrease but were still greater than concentrations of TON in the RW on March 17, 39 days after application (fig. 3). However, maximum concentrations of TON occurred immediately after fertilization and then decreased during the rising limb of the storm hydrograph. Elevated concentrations of TON after the February 10th storm event were most pronounced at peak flows (fig. 3). Rainfall records suggest that peak concentrations occurred just prior or shortly after the initiation of the February 10th storm event. The peak in TON concentrations almost immediately after fertilization indicate that the urea was reaching the outlet through channelized streamflow. Whether it reached the stream by both overland flow, caused by the heavy rainstorm, and direct application to non-perennial channels, or only by direct application to channels could not be determined. Aubertin and others (1973) also reported immediate rises in NH_3-N concentrations after fertilization and attributed this response to urea application directly into the stream channel.

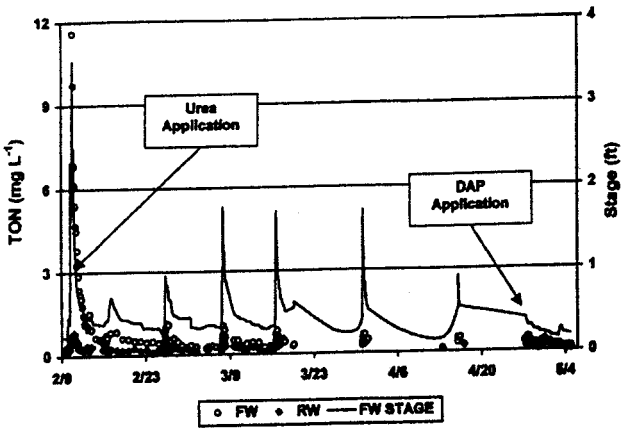

Figure 3—TON concentrations measured at the outlets of the fertilized (FW) and reference (RW) subwatersheds and stage at the outlet of the FW after urea fertilization (Values greater than 12 mg L^{-1} were not included in graph to better represent later trends in concentrations).

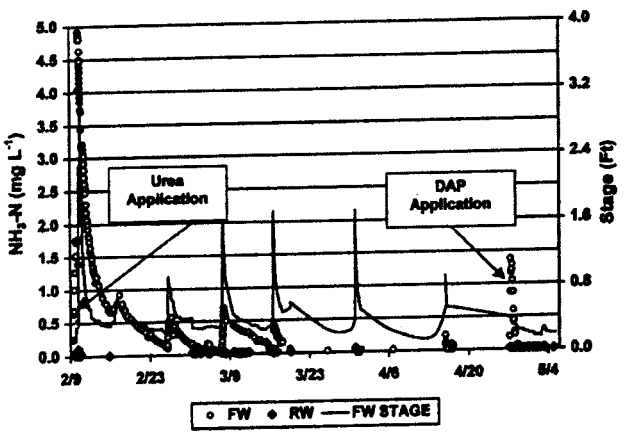

Figure 4—NH_3-N concentration at the outlets of the fertilized (FW) and reference (RW) subwatersheds and stage at outlet of the FW after urea fertilization.

As the hydrolization of the urea occurred, levels of NH_3-N increased. Concentrations of NH_3-N peaked at 4.91 mg L^{-1} approximately 24 hours after application during the February 10th storm event, corresponding closely to peak discharge. Concentrations continued to fall during base flow but rose during storms and generally followed the storm hydrograph. Ammonia-N concentrations at the FW outlet were elevated above those at the RW outlet until the middle of March, when TON levels had returned to pre-fertilization levels. Prior to the end of March, differences in NH_3-N levels between the FW and the RW were only discernable during storm runoff (fig. 4).

Nitrate-N concentrations showed a much different response to urea fertilization than did TON or NH_3-N (fig. 5). Concentrations rose slowly as nitrification occurred. The

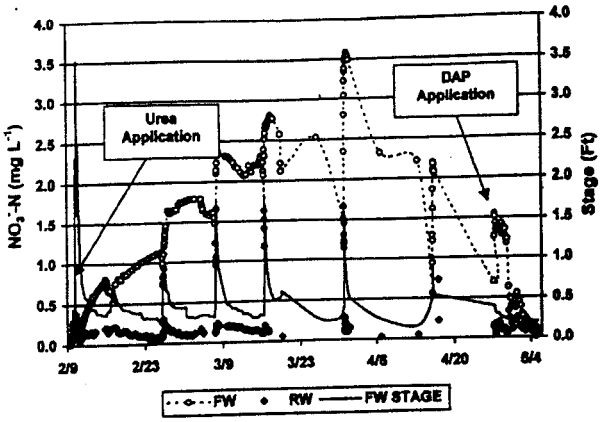

Figure 5—NO_3-N concentrations at outlet of the fertilized (FW) and reference (RW) subwatershed and stage at outlet of FW after urea fertilization.

peak concentration of 3.58 mg L^{-1} did not occur until 31 March, 50 days after urea application. Concentrations were still elevated when DAP was applied in April. Changes in NO_3^--N concentrations in response to storm events were also much different from those observed for TON and NH_3-N. Nitrate concentrations decreased during the rising limb and reached their minimal levels during peak storm discharges. Concentrations then increased rapidly during the falling limb of a storm hydrograph (fig. 5). Ammonia-N and TON concentrations generally increased during the rising limb, reached their maximum during or shortly after peak discharge, but then decrease during the falling limb. These results suggest that NO_3^--N concentrations during storms reflect a complex relationship between storm dilution of NO_3^--N, loss of NO_3^--N from soils, and alteration of nitrification rates due to changes in NH_4 availability or edaphic factors limiting nitrification.

Nitrate-N concentrations at the FW outlet were elevated beyond background levels for at least 77 days after urea fertilization. Mean concentrations prior to urea fertilization compared to mean concentrations during an approximate three week period prior to DAP fertilization in late April indicate that NO_3^--N concentrations were still 10-15 fold higher in the fertilized subwatershed than in the reference subwatershed (table 1). Low flow concentrations during the four hours just prior to DAP fertilization on April 27 averaged 1.25 mg L^{-1} at the FW outlet but only 0.13 at the RW outlet. As the result of the N contributed by the DAP fertilization, the potential alteration of NO_3-N levels by the urea fertilization in FW could not be quantified after this period. Ammonia-N and TON concentrations appeared to have returned to background values by the first of April prior to DAP application.

Increases in NH_3-N and NO_3^--N after urea fertilization were of a similar magnitude to those found by Abubertin and others (1973). However, the increases were greater than those reported after urea fertilization in the northwestern United States (Fredriksen and others 1975, Bisson 1982, 1988). The extremely severe rainstorm after application may

have contributed to the high levels of NH_3-N and NO_3^--N in the FW. However, differences in soils or vegetation among regions may also in part be responsible for these differences in N concentrations after fertilization.

DAP Application

Alteration of nitrogen concentrations in the FW as a result of DAP fertilization was less severe and of shorter duration than those found after urea fertilization (fig. 3-5). Elevated levels of NH_3-N were only evident for a 48 hour period after DAP fertilization. The maximum concentration was 1.37 mg L^{-1} and occurred approximately six hours after application. NH_3-N concentrations were again below detection limits as early as 30 hours after DAP application. TON concentrations also increased but were a result of the elevated concentrations of NH_3-N in the stream. Nitrate-N concentrations in the FW were not visibly increased after DAP application and remained constant or decreased during the interval between DAP application and the end of the study period.

The lack of any pronounced changes in N levels after the DAP application no doubt reflects the lower application rates of N. However, the storm-free period minimized off-site movement, while seasonal increases in temperatures and biological activity created greater uptake by plants and microbes. These factors may have decreased the percentage of total N export, further reducing in-stream N concentrations below those observed after the urea application.

Downstream Changes in N Concentrations

Application of fertilization in the FW did increase N levels at the outlet of the LGW. Increases beyond background levels were generally limited to periods when N was at its highest concentrations in the FW. Concentrations of NH_3-N and TON were greater at the outlet of LGW than the RW up to 3 days after urea application. Maximum concentrations of NH_3-N and TON at the outlet of the LGW were respectively 0.70 and 4.21 mg L^{-1} 24-26 hours after urea application.

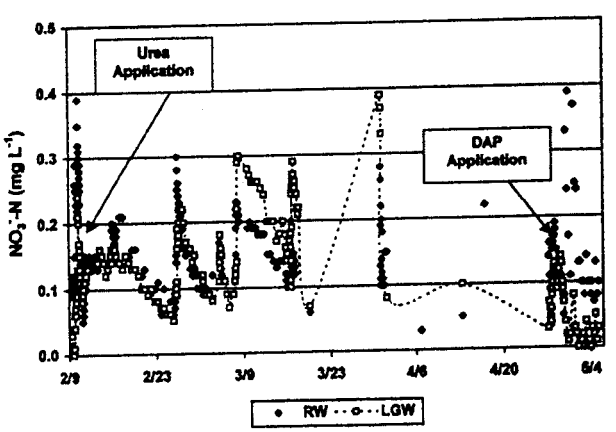

Figure 6—NO_3-N concentrations measured at the outlets of the reference subwatershed (RW) and the Little Glazypeau (LGW) watershed after urea fertilization.

Elevated concentrations of NO_3^--N at the LGW outlet were also evident (fig. 6). Elevated NO_3-N concentrations occurred later and over a greater time period than did NH_3-N and TON. Nitrate-N concentrations at the LGW were consistently lower than at the RW outlet prior to urea fertilization (table 1). Twenty-six days after urea fertilization, NO_3-N concentrations at the LGW outlet had risen and were greater than those measured at the RW outlet. Concentrations remained higher at the LGW than RW until March 31. Mean NO_3^--N concentrations during this time period were 0.24, 0.15, and 2.28 mg L^{-1} at the LGW, RW, and FW outlets respectively. These results suggest that NO_3^--N levels at the LGW outlet may have increased by as much as three or four fold after urea fertilization. There was no evidence of any alteration of NO_3^--N, NH_3-N, or TON concentrations (fig. 6) at the LGW outlet after DAP fertilization.

SUMMARY

Application of 437 kg ha^{-1} of urea significantly increased stream water N concentrations both within and downstream of the fertilized subwatershed. Ammonia-N and TON concentrations increased rapidly during and just after application and peaked within 24 hours of application at concentrations of 44.5 and 4.91 mg L^{-1} respectively. These increases, although dramatic, were relatively short-lived. It appeared that the elevated NH_3-N and TON concentrations in stream water shortly after urea application were due to the direct application of fertilizer on non-perennial stream channels and a 100-year storm event which occurred shortly after application. Increases of NO_3^--N concentrations as much as 10 times above background levels were observed. Increases were not as great as those for NH_3-N or TON but occurred over a greater duration of time. Nitrate-N concentrations in the fertilized subwatershed were still greater than background concentrations 77 days after urea application. Application of 140 kg ha^{-1} of DAP following urea application had minimal effects on N concentrations in the watershed. The lack of response was attributed to the lower amounts of applied N, lack of any significant storm events, and higher biologic activity during and following the DAP application.

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