

HOW MUCH NITROGEN IS THERE IN THE SPRING FROM FALL-APPLIED MAP, DAP, AND AMMONIUM SULFATE?

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Introduction

Diammonium phosphate (18-46-0) (DAP) and monoammonium phosphate (11-52-0) (MAP) are the two most common phosphorus (P) fertilizers in the US corn-belt. These granular fertilizers are excellent P sources because they are highly water-soluble, contain a high P concentration, and are easy to handle and store (Fixen, 1990). In addition, they represent a relatively low-cost source of supplemental N.

In much of the Corn Belt, it is a common practice to apply a blend of P and potassium (K) fertilizers during the fall. This time of application is favored because there is less potential for soil compaction (since soils tend to be drier than in the spring) and in general there is more time and equipment availability than during the busy planting season in the spring. One of the potential drawbacks of fall application of N-containing P fertilizers is that soil temperatures are warm (above 50°F) and nitrifying bacteria can quickly convert ammonium (NH_4^+) to nitrate (NO_3^-) (Alexander, 1965). Mulvaney (1994) showed that nitrification occurred in the order of urea [$\text{CO}(\text{NH}_2)_2$] > DAP > AMS [$(\text{NH}_4)_2\text{SO}_4$] > ammonium nitrate [NH_4NO_3] > MAP. The conversion to nitrate when fertilizers are applied well before crops will need N increase the risk of N loss through leaching or denitrification when soils are excessively wet in the spring. In laboratory studies, Mulvaney and Khan (1995) determined that denitrification decreased in the order of ammonia [NH_3] > urea > DAP > $(\text{NH}_4)_2\text{SO}_4$ > NH_4NO_3 > MAP. This differential in nitrification and denitrification rates are brought about by the fact that the hydrolysis (breakdown) of DAP increases soil pH, compared to MAP that lowers soil pH, and the nitrifying and denitrifying bacteria favor alkaline conditions (Lindsay et al., 1962; Allred and Ohlrogge, 1964; Firestone, 1982). Since DAP nitrifies faster than MAP and the resultant nitrate also denitrifies faster, it would appear that there would be less potential loss of N from MAP than DAP.

While substantial work has been done to compare the agronomic performance of MAP and DAP (Fixen, 1990), to our knowledge, there has been no attempt to evaluate N availability and efficiency from fall-N applications of MAP and DAP. Frequently, a 200 lb acre⁻¹ rate of material is applied which provides 22 lb N acre⁻¹ from MAP and 36 lb N acre⁻¹ from DAP. Agronomists have generally assumed that all N from fall application of MAP and DAP is fully available to the subsequent crop, but this has not been confirmed with research. Thus, the purpose of this study was to compare the efficacy of N from fall-applied versus spring-applied DAP, MAP, and AMS for corn (*Zea mays* L.) production. In addition, we conducted a laboratory study to measure the effect of soil water content on the rate of nitrification and denitrification of MAP and DAP.

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Materials and Methods

Incubation Study

An incubation study was conducted at Urbana, IL by mixing MAP and DAP with soil [Drummer silty clay loam soil (fine-silty, mixed, superactive, mesic Typic Endoaquolls)] at ratios of 70 and 140 mg N kg⁻¹ soil. The soil was collected from the field, sieved to pass a 2-mm screen, and then dried at 25°C for 5 days. The soil was rewet to 80% FC, and allowed to incubate for 2 weeks. The appropriate amount of fertilizer for each treatment was then added and mixed thoroughly. A 100-g sample was weighed into 24 individual plastic bags, enabling three replications and eight sampling dates for each treatment. The fertilizer-amended soil was incubated at constant room temperature (23°C ±2) at 80% FC for 2 weeks, after which half of the soil bags were incubated at 80% FC and the other half were incubated at 120% FC at room temperature. Samples were taken at 2-week intervals and frozen. Frozen samples were oven-dried to constant weight and were analyzed for NH₄⁺ and NO₃⁻. Total inorganic N (TIN) was calculated by adding NH₄⁺ and NO₃⁻ concentrations.

Field Study

A 3-year field experiment was conducted at Waseca, MN on Nicollet and Webster clay-loam Mollisols and at Urbana, IL on a Drummer silty clay-loam Mollisol. Both locations were tile-drained. All soil test levels except N were nonlimiting for crop grain yield.

At both locations a full factorial of three N sources (DAP, MAP, and AMS), two application times (fall and spring) and two N rates (40 and 80 lb N acre⁻¹) was replicated four times and arranged in a randomized, complete-block design. Treatment plots were 10 ft (4 rows) wide by 50 ft long. A simultaneous N rate study was conducted to develop N response curves. At Minnesota the study consisted of 0, 40, 80, and 170 lb N acre⁻¹ in 2004, with the high rate reduced to 120 lb N acre⁻¹ in 2005 and 2006. At Illinois, the N rate study consisted of fall- and spring-applied AMS at rates of 0, 40, 80, 120, 160, and 200 lb N acre⁻¹. At both locations triple super phosphate (0-46-0) was applied to all non MAP or DAP plots to eliminate the possibility of a differential response to P among the treatments. All treatments were broadcast-applied on fields with soybean [*Glycine max* (L.) Merr.] as the previous crop. In Minnesota, treatments were applied on 10 Nov. 2003, 24 Apr. 2004, 26 Oct. 2004, 4 May 2005, 1 Nov. 2005, and 12 Apr. 2006. In Illinois, treatments were applied 3 Nov. 2003, 5 Apr. 2004, 10 Nov. 2004, 6 Apr. 2005, 2 Nov. 2005, and 5 Apr. 2006. After treatment application the entire plot area was disked to 3-inch depth in the fall and field cultivated in the spring. Corn was planted on 30-inch row spacing. In Minnesota planting was done on 28 Apr. 2004, 4 May 2005, and 23 Apr. 2006. Corn hybrid and final plant populations were: NK N50-P5 at 34,000 plants acre⁻¹ in 2004; and Mycogen 2E522 at 33,000 plants acre⁻¹ in 2005 and 2006. In Illinois corn hybrid Pioneer 34B24 with final plant population of 30,200 plants acre⁻¹ for 2004 and 2005 and 29,600 plants acre⁻¹ for 2006 was planted on 29 Apr. 2004, 2 May 2005, and 8 May 2006. Corn was harvested on 19 Oct. 2004, 11 Oct. 2005, and 6 Oct. 2006 in Minnesota and on 17 Sep. 2004, 23 Sep. 2005, and 27 Sep. 2006 in Illinois.

Soil samples were collected from the top 6 inches approximately every 2 weeks after fall applications until soils froze. Sampling resumed after soils thawed, and continued until the middle of June, with spring samples taken at depths of 0 to 6 and 6 to 12 inches. The soil samples collected at the end of May were considered most important because this sampling represents the time immediately before the rapid N-uptake period of corn. Samples were analyzed for NO₃⁻-N and NH₄⁺-N concentration. Percent recovery of the applied N was estimated by subtracting N in

the control plot from that of the treated plots and dividing by the applied N rate (Pomares-Garcia and Pratt, 1978).

Soil N and grain yield data were analyzed using the MIXED procedure of SAS (SAS Institute, 2003) with year as random effect and location, N source, time of application, and N rate as fixed effects. The optimum N rate and yield at the optimum N rate was determined from the N rate study by regression analysis using PROC REG and PROC NLIN models (SAS Institute, 2003). Economic-optimum N rates (EONR) were calculated with an N: corn price ratio of 0.13. Statistical significance was declared at $p < 0.1$ unless otherwise indicated.

Results and Discussion

Incubation Study

Within the first 2 weeks of incubation at 80% FC, 74 and 87% of the N was nitrified for MAP and DAP, respectively (Fig. 1). Irrespective of N source, when soil moisture was below FC, the amount of NO_3^- was fairly constant for the rest of the incubation period. On the other hand, under water-saturated conditions, NO_3^- recovery dropped rapidly, especially during the first 2 weeks after soils were saturated. Similar results were observed for the 70 mg N kg^{-1} soil rate. These data indicate that N in MAP and DAP nitrified quickly at warm temperatures, and once N is nitrified, denitrification proceeded rapidly when soils are saturated with water.

Field Study

Weather and Soil Nitrogen

In Minnesota the soils were frozen from early December through late March in all 3 years while in Illinois, soils were frozen or at near freezing temperatures at the 4-inch depth during January and February of each year and in December 2004 and 2005 (Table 1). Temperature and precipitation were variable from year to year during the early spring and summer which impacted N loss potential and crop performance differently from year-to-year. A combination of warmer temperatures and wetter conditions than the average during some of the springs created very good conditions for leaching and denitrification, as it will be discussed later, while in other years the potential was very low.

Soil N levels in the field were largely unaffected by source of N or rate, thus the soil N recovery data presented were averaged across these variables (Fig. 2). Prevailing weather conditions in the early portion of the growing season were most important in determining N availability from the different times of fertilizer application, especially for fall applications. In general the spring application had greater potential for N recovery than the fall-applied treatments. For example, in Minnesota NH_4^+ recovery in early April from fall applications was very low in 2004, whereas recovery was approximately 30% in 2005 and 2006 (data not shown). Ammonium levels were low by late April in both 2005 and 2006, likely due to rapid nitrification under warm temperatures (Table 1), but NO_3^- recovery did not increase concomitantly, due to denitrification under warm, wet conditions or to leaching of nitrate to below sampling depth. Spring applications showed greater TIN recovery compared to fall applications, especially in 2005 when the spring application occurred in early May, later than in 2004 and 2006 (Fig. 2A). These findings indicate that reducing the amount of time between application and plant uptake could result in greater N recovery.

In Illinois, during the fall of 2003 there were low soil NH_4^+ and high soil NO_3^- levels (data not shown). In contrast, under similar average monthly temperatures in 2004 as in 2003, only 6 $\text{mg NO}_3^- \text{ kg}^{-1}$ was released during the first 20 days after application in 2004, compared to a release of 16 $\text{mg NO}_3^- \text{ kg}^{-1}$ in 2003, averaged across forms and rates of fertilizer. This differential carried through into April, with more NH_4^+ recovered in the top 6 inches of soil in the spring of 2005 than in the spring of 2004. Since by spring 2004 virtually all the fertilizer was nitrified, the trend in TIN recovery in Figure 2B mimics that for NO_3^- . Despite these differences in nitrification trends from the fall through the winter before the 2004 and 2005 cropping seasons, spring conditions were more important than winter conditions in determining recovery of applied N. March and April 2004 had excessive precipitation (Table 1) and little NO_3^- was recovered by mid-April; while drier conditions in 2005 provided low potential for denitrification and leaching and enhanced recovery of NO_3^- at a time when nitrification was taking place. Recovery trends for spring-applied fertilizer during the three years showed a rapid decline in NH_4^+ recovery concomitantly with an increase in NO_3^- recovery, reflecting nitrification (data not shown). Nitrification of the spring-applied fertilizer appeared to be essentially completed by the end of May in 2004 and 2006, while in 2005 nitrification continued into early June. Recovery of TIN by early June was low in 2004 and 2006 for both application times, probably as a result of substantial N uptake by the crop (Fig. 2B). In 2005, very low precipitation in May likely reduced both plant uptake of N and nitrate loss, resulting in greater TIN recovery in June. Greater NH_4^+ recovery in late April of all three years from spring- compared to fall-applied fertilizers seems to indicate that fertilizer applications in the spring could reduce the potential for denitrification or leaching by keeping the fertilizer in the NH_4^+ form during the spring, when N loss is typically most likely in the Midwest.

Nitrate recovery at the end of May from fall applications was about twice as great in a dry spring in 2006 relative to the previous two years (Fig. 3A). The dry spring in 2006 also improved relative recovery of the fall application compared to the spring application. Although no differences in percent TIN recovery were observed between fall applications in 2004 and 2005, substantially higher recovery of spring-applied N occurred in 2005 compared to 2004. Even though both years had periods with wet to saturated water conditions, the large difference was the result of less nitrification in 2005 since the soil remained mostly wet and cool between the time of N application and measurement of TIN. An additional factor may be that in 2005 the time elapsed between N application and soil TIN measurement was 15 days less than 2004. Nonetheless, these data show the impact early season weather conditions can have in the overall efficiency of fertilizers. The fact that N recovery was greater than 100% for the spring application in 2005 may also indicate that the fertilizer application had a priming effect in the mineralization of organic N present in the soil.

Soil TIN recovery was consistently greater for spring than for fall applications in Illinois (Fig. 3B). Regardless of the time of application, the largest fraction of the TIN recovered was NO_3^- . Although the early spring in 2004 was much wetter than in 2005, N recovery from the spring applications was similar for both years. Since 2005 was dryer, there was less nitrification potential as reflected in the larger proportion of NH_4^+ in TIN. Nonetheless, the fact that 2004 and 2005 had similar TIN is indicative of the fact that spring applications have greater potential for N recovery even when substantial nitrification had taken place. Conversely, wet conditions in 2004 likely caused nominal recovery of the fall-applied N, while dry conditions in 2005 helped increase recovery of the N applied in the fall. This finding indicates that spring-applied N has greater potential for recovery than fall-applications, and precipitation patterns in the spring have an important impact on the efficiency of fall N applications. Averaged across 3 years in Illinois, 35% of the fall-applied N was recovered as inorganic N compared to 90% for the spring application.

Grain Yield

In Minnesota, response curves generated from the full N rate studies indicated that the EONR from a spring application of AMS averaged across all 3 years was 137 lb N acre⁻¹, which produced a yield of 181 bu acre⁻¹. At this location, typical application rates (200 lb acre⁻¹) of MAP or DAP would have produced no yield reduction compared to the yield at the EONR, given that there was full recovery of TIN from the soil at the end of May. In Illinois, the EONR and the yield at the EONR were 138 lb N acre⁻¹ and 179 bu acre⁻¹ for fall AMS application and 158 lb N acre⁻¹ and 192 bu acre⁻¹ for spring AMS application. In typical field situations, in which MAP or DAP are a minor source of N, unrecovered N from the use of fall-applied MAP or DAP would reduce N supply at the flatter portion of the response curve. For this reason, N loss from fall-applied MAP or DAP would typically result in minimal impact on yield. Averaging percent soil N recovery in Illinois (data in Fig. 3B) indicated that from a typical application, 23 lb from a 36 lb DAP-N acre⁻¹ application and 14 lb from a 22 lb MAP-N acre⁻¹ application were not recovered by the end of May following fall applications. Subtracting 23 and 14 lb of N from the EONR translated into a yield loss of 4 bu acre⁻¹ (2.4% of the yield at EONR) for DAP and 2 bu acre⁻¹ (1.3% of the yield at EONR) for MAP. Yield losses from loss of N from spring-applied MAP and DAP were very minor.

In Minnesota, source of N produced no significant yield difference. Yields were higher with N than without N, indicating that N was limiting in the study (Fig. 4). Averaged over the 3 years, the 80 lb N acre⁻¹ rate produced 14% greater yield than the 40 lb N acre⁻¹ rate. The response to application time was influenced by year. Spring applications resulted in 8% greater yield relative to fall applications in 2004 and 13% greater yields for the spring compared to the fall application in 2005. On the other hand, in 2006 fall-N application produced a 5% greater yield than spring application. Low precipitation during the early spring, when potential for N loss is typically greater, likely improved N recovery from the fall-applied fertilizers in 2006. Further, good growing season conditions likely induced substantial mineralization of organic nitrogen throughout the growing season resulting in the highest yields during this 3-year study. Percent TIN recovery at the end of May for the spring application in 2005 was 2.2 times higher than that of 2006 (Fig. 3A). However, the 2006 crop had overall better growing season conditions resulting in 24% greater yield for spring-N applications than the 2005 season (Fig. 4). This illustrates the fact that overall growing season conditions can overwhelm any N management effects or what may be expected in terms of grain yield by measurements of soil TIN recovery before rapid crop growth.

Corn grain yield in Illinois was not affected by N source or any of the interactions of main effects, but significant differences were observed for rate and time of application, thus the data were averaged across N source (Fig. 4). The 80 lb N acre⁻¹ rate produced 15% greater yield than the 40 lb N acre⁻¹ rate. Averaged over N rate and source, spring-N application resulted in a 7% yield increase relative to fall application. The fact that the 40 lb N acre⁻¹ rate applied in the spring produced similar yields to the 80 lb N acre⁻¹ rate applied in the fall for 2005 and 2006 indicates an advantage for spring applications. On the other hand, there was no yield difference for time of application in 2004. In 2004, growing-season conditions likely induced ample N availability by increasing mineralization of soil N. This likely compensated for the low N recovered from the fall application. The yield and TIN recovery data (Fig. 4 and Fig. 3B, respectively) illustrate that overall growing season conditions can overshadow the effect of early-season soil N status. For the spring application in 2004 and 2005, percent TIN recovery was very similar; but overall better growing season conditions in 2004 resulted in 46 bu acre⁻¹ (32%) greater yields for spring-N applications than in 2005.

Conclusions

The incubation study showed rapid nitrification rates, regardless of whether the NH_4^+ was in MAP or DAP. Once in NO_3^- form, the rate of denitrification was influenced by soil water conditions. Nitrate concentrations remained constant in the soil if water content was below FC, but denitrification proceeded quickly once soils were saturated.

Soil inorganic N and grain yield were not affected differently by N source (DAP, MAP, and AMS) at both field locations. The fact that grain yield increased with increasing N rates clearly indicated that N was limiting in the study.

In general, agronomists have assumed that most or the entire amount of N from ammoniated phosphates is available to the crop the following year when applications are done late in the fall, when soil temperatures are low enough to slow nitrification rates. This study indicates that such an assumption is inaccurate in most years. At the end of May, fall-applied N recovery as inorganic N from the soil prior to the rapid N uptake period of corn was 31% in Minnesota and 35% in Illinois. In years in which soils are warm and become water-saturated after substantial nitrification of NH_4^+ , leaching and denitrification can result in nearly all of the N from fall-applied MAP or DAP to be unrecovered. However, since a typical 200 lb acre⁻¹ rate of MAP and DAP amounts to only 22 and 36 lb N acre⁻¹, respectively, the low recovery of N from a fall application would reduce N supply at the less responsive portion of the N response curve. Our results indicated that at most, the reduction from EONR yield is close to 3%. This study provides evidence that regardless of rate or source, the fate of fall- and spring-applied N is mostly impacted by weather conditions in early spring. Further, even if the early spring was conducive to lower N recovery, adequate crop-growing conditions for most of the remainder of the season compensated in part, likely through mineralization, for some of the unrecovered N from ammoniated phosphates in the early season.

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Table 1. Air temperature and rainfall for a 30-year period (averaged from 1971 to 2000) and for the period fall-summer from fall 2003 to summer 2006 in Minnesota and Illinois.

Month	Minnesota						Illinois									
	Air temperature (°F)			Precipitation (inch)			Air temperature (°F)			Precipitation (inch)						
	30-yr	03-04	04-05	05-06	30-yr	03-04	04-05	05-06	30-yr	03-04	04-05	05-06				
Oct.	48.0	49.3	49.6	52.0	2.5	0.7	2.4	1.3	54.9	54.9	54.9	56.3	2.8	1.3	3.7	1.3
Nov.	31.8	32.0	37.4	36.3	2.3	1.2	1.2	1.8	41.9	45.1	45.5	44.1	3.5	5.0	5.2	3.7
Dec.	17.2	23.4	22.5	14.7	1.4	1.3	0.2	1.1	30.2	33.4	32.4	25.2	2.8	3.1	2.0	1.9
Jan.	11.3	17.2	14.4	26.6	1.4	0.4	1.1	1.0	25.0	24.4	28.2	38.3	1.9	2.2	6.2	1.8
Feb.	18.3	18.5	25.3	17.8	0.9	1.6	1.4	0.5	30.2	30.4	35.1	31.3	2.0	0.6	2.0	0.5
Mar.	30.7	36.3	29.8	31.8	2.5	2.8	2.9	2.8	41.0	44.4	38.7	42.3	3.2	7.8	1.7	3.5
Apr.	45.3	49.1	51.6	51.4	3.2	1.8	3.4	4.4	52.0	54.3	55.0	57.0	3.7	10.9	4.0	4.4
May	58.8	57.4	55.4	60.1	4.0	5.6	5.9	2.8	63.3	66.0	61.7	62.4	4.8	4.4	1.0	3.1
June	68.2	65.3	73.0	69.1	4.2	6.4	5.7	5.2	72.3	70.0	75.4	71.8	4.2	3.8	2.4	1.7
July	71.6	70.0	73.9	75.0	4.5	7.1	3.1	3.7	75.6	73.0	76.5	77.0	4.7	5.7	4.3	7.8
Aug.	69.3	64.6	69.6	71.1	4.6	5.7	4.5	5.1	73.6	68.7	76.1	74.3	4.4	3.6	2.2	3.0
Sep.	60.6	66.0	65.5	58.5	3.2	6.9	7.0	4.4	66.7	68.9	71.2	64.9	3.2	2.2	5.7	3.2
Total					34.7	41.5	38.8	34.2	41.1	50.4	40.4	50.4	41.1	50.4	40.4	35.8

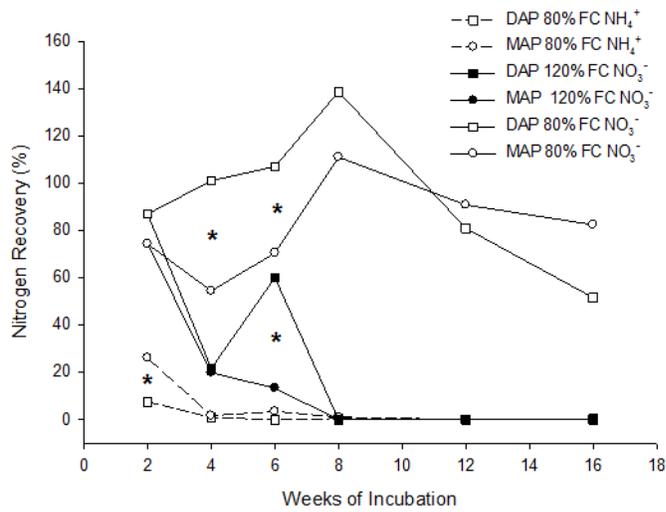


Figure 1. Apparent recovery of ammonium-N (NH₄⁺-N) and nitrate-N (NO₃⁻-N) from soil receiving 140 mg N kg⁻¹ from MAP or DAP incubated at room temperature at 80% or 120% field capacity (FC) water content. * Between two N recovery levels at a specific sampling time indicates a significant difference.

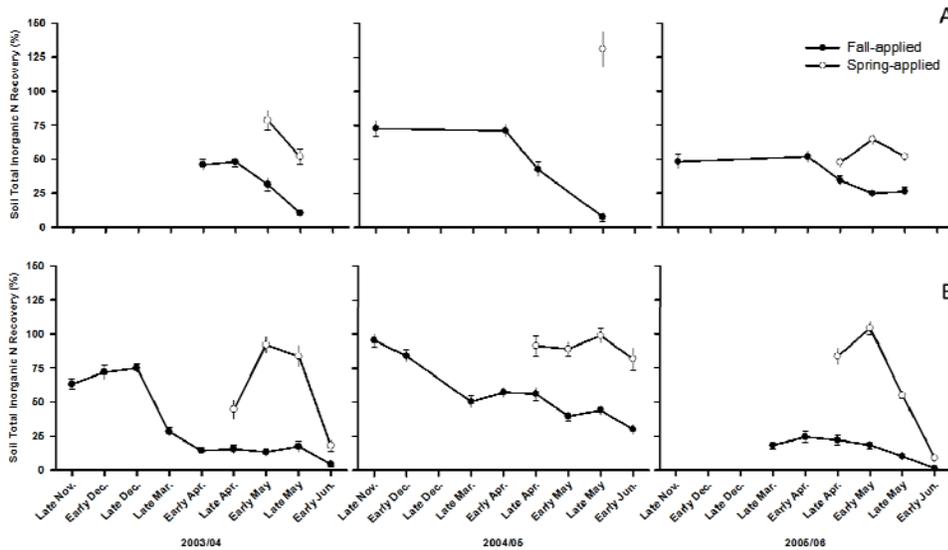


Figure 2. Apparent recovery of total inorganic N (ammonium plus nitrate) at different sampling times in the top 6 inches of the soil for three growing seasons averaged across N source and rate for fall and spring application times for Minnesota (A) and Illinois (B). Bars represent standard error of the mean ($n=24$).

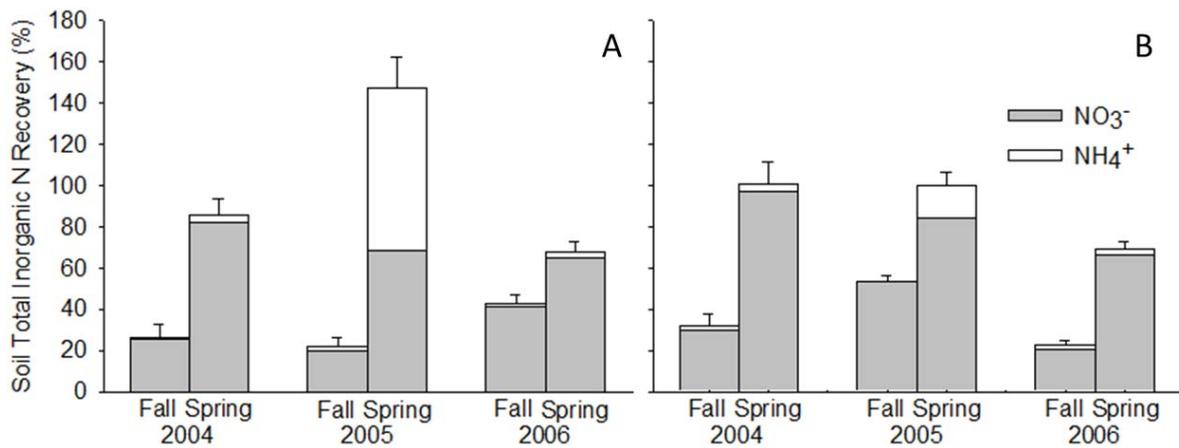


Figure 3. Apparent recovery of total inorganic N (ammonium plus nitrate) in the top 12 inches of the soil at the end of May for three growing seasons averaged across N source and rate for fall and spring application times for Minnesota (A) and Illinois (B). Bars represent standard error of the mean ($n=24$).

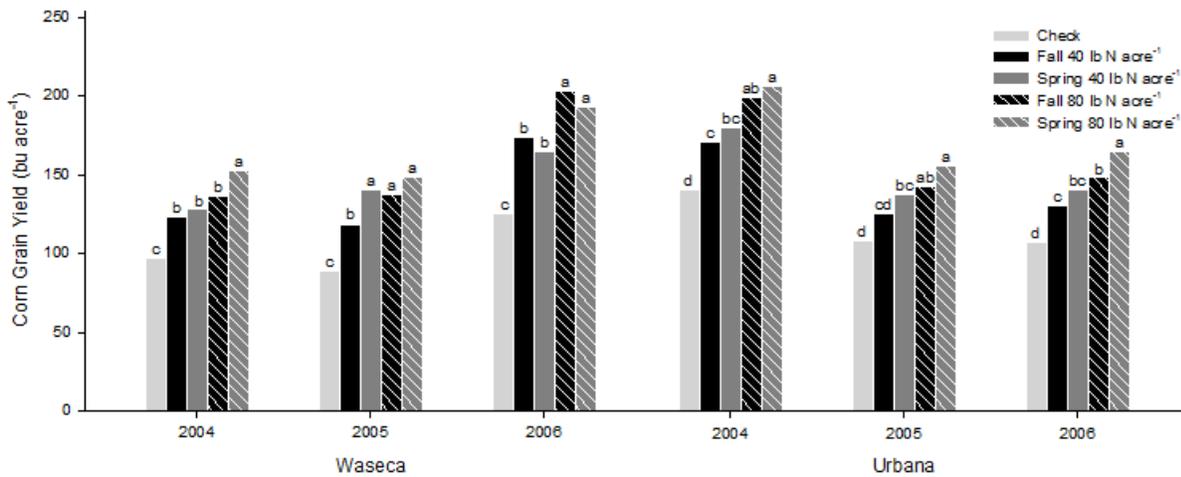


Figure 4. Corn grain yield in each year and location averaged across N source for the 40 and 80 lb N acre⁻¹ rate and the fall and spring application times. Within location and year, yields with the same letter are not significantly different ($p > 0.05$).