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Macronutrients in soil and bromegrass after long-term N fertilization

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Abstract

Information on the long-term impact of repeated annual fertilizer applications of different nitrogen (N) sources on soil and plants is needed to develop sustainable grassland production systems. The concentration of macronutrients in the 0–5, 5–10, 10–15, 15–30, 30–60, 60–90 and 90–120 cm layers in a thin Black Chernozemic (Typic Boroll) soil and in bromegrass (*Bromus inermis* Leyss.) hay were compared after 15 annual applications of 168 and 336 kg N ha^{-1} as ammonium nitrate, urea, calcium nitrate, and ammonium sulphate, and a zero-N check. The concentration of NO_3-N was increased by ammonium nitrate and ammonium sulphate at both N rates in most soil layers, by calcium nitrate at both N rates and by urea at 336 kg N ha^{-1} in the 15-60 cm soil. The accumulation of NO_3-N increased with soil depth down to 60 cm, except for urea and ammonium sulphate at 168 kg N ha^{-1}, and then it declined in deeper soil layers. The concentration of NH_4-N was increased with fertilizer applications in some of the surface soil layers. The concentration of P was increased in the top 15 cm soil by ammonium nitrate and ammonium sulphate. The concentrations of Ca, Mg and K in the surface soil declined with most of the N fertilizer treatments while some treatments increased the Ca and Mg concentrations in the deeper soil layers. Increasing the N rate from 168 to 336 kg N ha^{-1} usually accentuated the above stated N effects on the concentration of macronutrients in the soil. The nitrate-based fertilizers caused more accumulation of NO_3-N in some soil layers than the ammonium-based fertilizers. The relative increase in the concentration of NH_4-N and P and the decline in the concentration of Ca, Mg and K in the soil by N addition was usually associated with the concomitant lowering of soil pH by N fertilization. In bromegrass hay, the total N concentration was increased by N fertilization but the concentration of other elements, except K, usually declined because of the dilution effect of the extra hay yield associated with N addition. Increasing the N rate from 168 to 336 kg N ha^{-1} further elevated the total N concentration but had no effect on the concentration of the other elements. Total N concentration in the hay tended to be greater with ammonium sulphate and ammonium nitrate than with the other 2 fertilizers. The concentration of total S was greater with ammonium sulphate than the other N fertilizers, and the concentration of P, Ca, Mg and K was not affected by the N fertilizer type. Fertilizer-induced high levels of NO_3-N, NH_4-N and P in soil may present potential for environmental pollution at these high N rates.

Key Words: concentration, forage, N source, rate of N

Resumen

Para desarrollar sistemas de producción sostenibles en pastizales se necesita información del impacto a largo plazo sobre el suelo y las plantas de las aplicaciones anuales repetidas de diferentes fuentes de nitrógeno (N). La concentración de macronutrientes en los estratos de 0–5, 5–10, 10–15, 15–30, 30–60, 60–90 y 90–120 cm de un suelo delgado negro Chernozem (Typic Boroll) y en el heno de "Bromegrass" (*Bromus inermis* Leyss.) se compararon después de 15 aplicaciones anuales de 168 y 336 kg N ha^{-1} como nitrato de amonio, urea, nitrato de calcio, sulfato de amonio y de un control de cero-nitrógeno. La concentración de NO_3-N se incremento en la mayoría de los estratos de suelo por la aplicación de nitrato de amonio y sulfato de amonio a ambas tasas de aplicación y en la profundidad de 15-60 cm por la aplicación de nitrato de calcio a ambas tasas de aplicación y por la de urea a 336 kg N ha^{-1}. La acumulación de NO3-N aumentó con la profundidad del suelo hasta los los 60 cm, excepto para la urea y el sulfato de amonio a 168 kg N ha^{-1}, después disminuyó en las capas mas profundas del suelo. En algunas capas del suelo la concentración de NH_4-N aumento con la aplicación de fertilizante. La concentración de P en los primeros 15 cm del suelo se incremento con la aplicación de nitrato de amonio y sulfato de amonio. Las concentraciones de Ca, Mg y K en la superficie del suelo disminuyeron con la mayoría de los tratamientos de fertilización nitrogenada, mientras que algunos tratamientos incrementaron las concentraciones de Ca y Mg en las capas profundas del suelo. El aumentar la cantidad de nitrógeno de 168 a 336 kg N ha^{-1} usualmente acentuó los efectos del N descritos previamente sobre la concentración de los macronutrientes del suelo. Los fertilizantes a base de nitrato causaron una mayor acumulación de NO_3-N en algunas capas del suelo que la obtenida con los fertilizantes a base de amonio. El incremento relativo en la concentración de NH_4-N y P y la disminución de la concentración de Ca, Mg y K en el suelo por la adición de N usualmente se asocio con la concomitante baja del pH del suelo por la fertilización nitrogenada. En el heno de "Bromegrass"la concentración total de N se incremento con la fertilización nitrogenada, pero la concentración de otros elementos, excepto K, usualmente disminuyo debido al efecto de dilución de un mayor rendimiento de heno asociado con la aplicación de N. Aumentar la tasa de aplicación de 168 a 336 kg N ha^{-1} elevó más la concentración de N pero no tuvo efecto en la concentración de los otros elementos. La concentración de N total en el heno tendió a ser mayor con el sulfato de amonio y el nitrato de amonio que con los otros dos fertilizantes. La concentración total de S fue mayor con el sulfato de amonio que con los otros fertilizantes nitrogenados y la concentración de P, Ca, Mg y K no fue afectada por el tipo de fertilizante nitrogenado. Los altos niveles de NO_3-N, NH_4-N y P en el suelo inducidos por los fertilizantes pueden presentar un problema potencial de contaminación con estas altas tasas de N.

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Nitrogen (N) fertilization is essential to sustain high yields of managed forage grasses in the Canadian prairies. The effect of N on forage grass production (Campbell et al. 1986, Malhi et al. 1986, 1992, Ukrainetz and Campbell 1988, and soil acidification (Hyot and Hennig 1982, Mahler and Harder 1984) have been shown to vary with the type of N fertilizer applied. Ammonium sulphate, ammonium nitrate and urea (in a decreasing order) reduce soil pH (Adams 1984, Harapiak et al. 1992). Earlier studies also suggested that the magnitude of change in soil pH and nutrient concentration depends on the rate of N fertilizer applied (Malhi et al. 1991) for data collected after 16 years. Limited information is available on the long-term effects of N sources and rates on the concentration of macronutrients in the Canadian prairie grasslands. The objective of the investigation was to determine the long-term effects of different rates and sources of N on the concentration of macronutrients at different depths in the soil and in the bromegrass hay.

Materials and methods

The study was conducted near Crossfield, Alberta, Canada (5°E30' N 114E°3' W) on a thin Black Chernozemic soil (Typic Boroll) with 9.5% organic matter and a loam texture. The 30-year mean annual precipitation of the area is 478 mm with two-thirds of the precipitation normally received in the growing season from May to September (Environment Canada).

Nine treatments were applied with 4 N fertilizers (ammonium nitrate, urea, calcium nitrate, and ammonium sulphate), each applied at 2 rates (168 and 336 kg N ha^{-1}) plus a zero-N check. Six replications of 3 m x 3 m treatment plots were arranged in a randomized complete block design. The experiment began in 1979. Bromegrass (*Bromus inermis* Leyss) was grown for hay and the stand was maintained during the study period, cut once in mid to late July of each year and another time later if there was sufficient regrowth. The N fertilizers were surface-broadcast annually in mid to late April.

For hay samples, all of aboveground bromegrass plant was harvested at 5 cm height above soil surface in July 1993, dried at 65° C and ground to pass through a 1-mm sieve. To determine the total N and P in the hay, the samples were subjected to the Kjeldahl procedure using hot H_2SO_4 and their concentrations in the digests were measured by a Technicon AutoAnalyzer II (Technicon Industrial Systems 1977). Determination of total K, Ca, Mg and S in the hay was done by digesting the samples in a mixture of nitric acid and perchloric acid and the concentrations in the digests were determined by inductively coupled plasma (ICP) emission spectrometry.

Soil samples, composite of 10 cores, from the 0–5, 5–10, 10–15, 15–30, 30–60, 60–90 and 90–120 cm depths in each plot were obtained in the autumn of 1993, using a 2.4 cm diameter coring tube with a hydraulic sampler. The soil horizons Ap, Ah, Bm and C constitute approximately 0–10, 10–15, 15–40 and > 40 cm of the soil depths, respectively. The samples were air dried at room temperature and ground to pass through a 2-mm sieve. A 1:5 soil:2M KCl solution ratio was used to extract NH_4-N and NO_3-N. Phosphorus was extracted using a modified procedure of Miller and Axley (1956) by shaking 10 g soil in 50 ml of 0.03M NH_4F + 0.015M solution H_2SO_4 for 10 minutes. The concentrations of NH_4-N, NO_3-N and P in the extracts were determined by a Technicon AutoAnalyzer II (Technicon Industrial Systems 1973a, 1973b, 1977). The Ca, Mg and K were extracted using a 1:20 soil:1M ammonium acetate solution (pH 7.0) ratio and the concentrations in the extracts were measured by ICP.

The data for each soil layer and bromegrass hay were subjected to analysis of variance (ANOVA) in GLM (SAS Institute Inc. 1989) and the least significant difference ($LSD_{0.05}$) was used to determine significant differences between the treatments. Data for different soil layers were analysed separately.

Results and discussion

Macronutrients in Soil

Nitrogen addition and rate effects. The addition of ammonium sulphate substantially increased the NO_3-N concentration in the top 15 cm of the soil at 168 kg N ha^{-1}, and down to the 120 cm soil depth at 336 kg N ha^{-1} (Table 1). Application of ammonium nitrate and calcium nitrate at 336 kg N ha^{-1} significantly increased NO_3-N concentration in all soil layers. The NO_3-N concentration was tremendously increased by a change in the N rate from 168 to 336 kg N ha^{-1} in all soil layers with ammonium nitrate and ammonium sulphate, in the 30-120 cm soil with urea, and in the 10-120 cm soil with calcium nitrate.

The NH_4-N concentration in the 0-5 cm soil was markedly increased by ammonium nitrate, calcium nitrate and ammonium sulphate applications at both N rates. The NH_4-N concentration was also significantly increased in the 5-10 cm layer by ammonium sulphate at both N rates and by ammonium nitrate at 336 kg N ha^{-1}, and in the 10-15 and 15-30 cm layers by ammonium sulphate at 336 kg N ha. Urea did not change the NH_4-N concentration significantly. Changing the N rate from 168 to 336 kg N ha^{-1} increased the NH_4-N concentration in the top 10 cm of soil with AN and in the top 30 cm of the soil with ammonium sulphate. The depth of NH_4-N accumulation in the present investigation was greater than that observed in another experiment on the same site with 112 kg N ha^{-1} (Harapiak et al. 1992). The accumulation of NH_4-N in the soil was most likely associated with the depression in pH from different N sources (Malhi et al. 2000). No significant effect of the fertilizer treatments was observed on the NH_4-N concentration in soil below the 30 cm soil layer.

Though no statistical analysis was done to compare the concentration of macronutrients in different layers, the large changes in the NO_3-N and NH_4-N concentrations with the change in soil depth are pointed out in the following discussion. At both N rates of calcium nitrate and ammonium nitrate, and at 336 kg N ha^{-1} rate of urea and ammonium sulphate, the NO_3-N concentration showed a trend of increase with soil depth down to the 30-60 cm layer and then to decline with increase in soil depth. Also, the difference in NO_3-N concentration between the 168 and 336 kg N ha^{-1} rates increased from the 0-5 cm layer (range of –3.3 to 15.1 mg kg^{-1}) down to the 30-60 cm layer (range of 28.5 to 333.3 mg kg^{-1}) and then declined in the deeper soil layers. The zone of maximum NO_3-N concentration (30–60 cm) at the 168 and 336 kg N ha^{-1} in the present study was deeper than the earlier observations (15–30 cm) at the same site in another experiment with 112 kg N ha^{-1} (Harapiak et al. 1992). This appears to be due to a combination of higher rates of N application for a longer period.

At 168 kg N ha^{-1} rate, extractable P concentration was significantly increased by ammonium nitrate in the top 5 cm of the soil and by ammonium sulphate in the top 10 cm of soil. The concentration of extractable P in the top 15 cm of soil was tremendously increased by ammonium nitrate and ammonium sulphate at 336 kg N ha^{-1} over the check as well as over the 168 kg N ha^{-1}. Urea and calcium nitrate did not influence the P concentration in

Table 1. Influence of 15 annual applications of 4 N sources at 2 rates to bromegrass on the concentration of macronutrients in different layers of a thin Black Chernozemic soil at Crossfield, Alberta, Canada.

Rate of N ($kg N ha^{-1}$)	Source of N[a]	Concentration of macronutrients in different soil layers (cm) 0-5	5-10	10-15	15-30	30-60	60-90	90-120
				NO_3-N ($mg kg^{-1}$)				
0	Check	1.5	0.6	0.5	0.8	1.1	0.8	1.2
168	AN	2.0	4.3	5.3	26.8	27.5	5.9	1.5
	Urea	3.7	0.8	1.0	2.0	2.0	0.8	0.3
	CN	4.7	2.4	1.9	32.0	50.7	16.2	1.5
	AS	20.7	13.0	13.2	12.2	5.8	6.1	1.5
336	AN	17.1	23.8	32.9	154.3	268.8	112.4	18.8
	Urea	1.4	0.8	1.9	15.2	30.5	18.1	4.5
	CN	9.9	8.2	12.0	218.2	384.0	132.1	16.1
	AS	29.4	33.1	51.4	92.5	112.8	86.2	35.4
$LSD_{0.05}$		7.3	7.6	9.4	42.3	56.7	37.3	12.5
				NH_4-N ($mg kg^{-1}$)				
0	Check	13.4	11.0	8.8	8.2	6.2	4.3	4.4
168	AN	42.1	20.1	10.2	7.5	6.0	4.6	5.8
	Urea	26.4	13.6	8.4	6.1	5.9	5.0	5.6
	CN	35.5	14.6	9.5	9.4	5.6	4.5	5.6
	AS	58.0	45.9	14.4	8.4	5.6	4.3	4.8
336	AN	94.0	50.9	14.7	9.8	8.5	6.1	6.0
	Urea	29.5	15.8	10.3	7.0	6.4	5.1	5.7
	CN	34.2	14.5	10.0	9.8	6.7	4.4	4.2
	AS	183.7	252.0	162.8	47.1	6.5	5.2	5.5
$LSD_{0.05}$		18.1	18.3	18.2	8.6	ns	ns	ns
				P ($mg kg^{-1}$)				
0	Check	9.6	4.3	3.0	0.6	0.0	0.0	0.0
168	AN	13.8	3.7	2.4	0.1	0.2	0.0	0.0
	Urea	7.7	2.4	1.5	0.3	0.0	0.0	0.0
	CN	7.1	2.8	1.3	0.2	0.0	0.0	0.0
	AS	29.9	9.2	1.6	0.3	0.3	0.0	0.0
336	AN	28.6	11.8	24.4	0.2	0.2	0.0	0.0
	Urea	8.8	2.9	1.5	0.2	0.2	0.0	0.0
	CN	5.8	2.3	1.1	0.0	0.3	0.0	0.0
	AS	36.8	34.1	14.8	0.8	0.0	0.0	0.0
$LSD_{0.05}$		3.9	2.9	1.8	0.4	ns	ns	ns
				Ca ($mg kg^{-1}$)				
0	Check	2763	2971	2625	2668	2646	2406	1948
168	AN	1347	2903	2679	2714	2671	2645	2398
	Urea	1924	2870	2672	2676	2784	2634	2139
	CN	2989	3507	2856	2763	2788	2170	1933
	AS	568	2091	2738	2753	2706	2406	2168
336	AN	509	1610	2658	2775	2996	2600	2136
	Urea	1809	2727	2750	2728	2725	2541	2168
	CN	2939	3582	2938	2894	2727	2217	1938
	AS	287	588	2017	3027	3128	2304	1970
$LSD_{0.05}$		370	348	222	108	222	ns	Ns

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Rate of N (kg N ha^{-1})	Source of N[a]	Concentration of macronutrients in different soil layers (cm) 0-5	5-10	10-15	15-30	30-60	60-90	90-120
					Mg (mg kg^{-1})			
0	Check	445	498	571	594	660	759	925
168	AN	183	406	540	543	640	694	734
	Urea	280	443	569	550	656	792	889
	CN	124	228	388	593	767	901	1041
	AS	82	208	367	552	708	808	975
336	AN	84	171	384	520	703	838	917
	Urea	214	344	480	549	662	769	922
	CN	72	84	142	465	860	974	1040
	AS	58	61	120	426	924	977	1076
$LSD_{0.05}$		27	34	35	44	138	ns	ns
					K (mg kg^{-1})			
0	Check	476	323	279	258	234	184	172
168	AN	272	198	199	211	245	175	165
	Urea	244	182	198	188	217	176	176
	CN	406	243	202	188	201	174	187
	AS	344	224	177	183	211	171	172
336	AN	372	271	229	194	231	191	187
	Urea	265	184	189	205	257	170	169
	CN	484	320	222	181	198	161	171
	AS	323	269	231	213	216	173	178
$LSD_{0.05}$[b]		50	39	34	34	ns	ns	ns

[a]AN, CN and AS refer to ammonium nitrate, calcium nitrate and ammonium sulphate, respectively.
[b]The $LSD_{0.05}$ value is given when the F-test was significant and ns is given when the F-test was not significant.

any soil layer and no fertilizer influenced the P concentration in the soil below the 15 cm depth. Increased P concentration in the soil was related to greater soil acidification by ammonium sulphate and ammonium nitrate relative to the other fertilizers (Malhi et al. 2000). Harapiak et al. (1992) reported strong negative correlation between the soil pH and soil P concentration, at the same site in a different experiment.

Unlike NO_3-N, NH_4-N and P, the concentration of extractable Ca was reduced in the 0–5 cm layer by ammonium nitrate, urea and ammonium sulphate at both N rates, in the 5–10 cm layer by ammonium sulphate at both N rates and ammonium nitrate at 336 kg N ha^{-1}, and in the 10–15 cm layer by ammonium sulphate at 336 kg N ha^{-1}. Another noticeable effect of ammonium nitrate and ammonium sulphate applications was a higher Ca concentration than the check treatment at 336 kg N ha^{-1} with ammonium sulphate in the 15–30 and 30–60 cm layers and with ammonium nitrate in the 30–60 cm layer. With an increase in the N rate from 168 to 336 kg N ha^{-1}, the concentration of extractable Ca declined in the 0–5 and 5–10 cm layers with ammonium nitrate and the 5–10 and 10–15 cm layers with ammonium sulphate. However, it was increased in the 30–60 cm layer with ammonium nitrate, in the 15–30 cm layer with calcium nitrate and in the 15–30 and 30–60 cm layers with ammonium sulphate. It appears that ammonium nitrate and ammonium sulphate displaced Ca from the shallower soil layers, which accumulated in the deeper soil layers. Application of calcium nitrate (which contains Ca) on the other hand significantly increased the Ca concentration in the 5-10 and 10–15 cm layers at both N rates, and in the 15–30 cm layer at 336 kg N ha^{-1}.

The concentration of extractable Mg was markedly decreased by all of the N treatments in the 0-5 and 5-10 cm layers, by all N fertilizers at 336 kg N ha^{-1} and by calcium nitrate and ammonium sulphate at 168 kg N ha^{-1} in the 10–15 cm layer, and by all N treatments except calcium nitrate at 168 kg N ha^{-1} in the 15–30 cm layer. On the other hand, calcium nitrate and ammonium sulphate at 336 kg N ha^{-1} significantly increased the Mg concentration in the 30–60 cm layer. When the N rate was increased from 168 to 336 kg N ha^{-1}, the concentration of extractable Mg declined in the top 15 cm of the soil with AN and urea, and in the top 30 cm of the soil with calcium nitrate and ammonium sulphate, while a significant increase in the Mg concentration was observed in the 30-60 cm layer with ammonium sulphate. The Mg concentration in the soil below the 60 cm depth did not show any response to the N treatments.

The concentration of extractable K in the top 30 cm of the soil, except for the top 10 cm of the soil with calcium nitrate at 336 kg N ha^{-1}, was significantly reduced by all N treatments. But with a change in the N rate from 168 to 336 kg N ha^{-1}, the concentration of extractable K was significantly increased in the top 10 cm of the soil by ammonium nitrate and calcium nitrate as well as in the 5–10 and 10–15 cm layer by ammonium sulphate. The K concentration in the deeper soil layers did not respond to any of the N treatments.

At both 168 and 336 kg N ha^{-1} rates, increased NO_3-N, NH_4-N and P concentrations in the surface soil suggested greater potential for their loss through surface water runoff, denitrification and ammonia volatilization, while accumulation of NO_3-N in the deeper soil layers increased the potential for its leaching to groundwater. The trend towards decreased Ca, Mg and K concentrations in the shallower soil associated with most N treatments was considered to be the direct result of a greater uptake of these elements in higher yielding bromegrass hay as a result of fertilization with N. The increased concentration of Ca in these soil layers associated with the application of calcium nitrate occurred due to the fact that Ca addition was taking place But, an increased concentration of Ca and/or Mg in the deeper soil with some ammonium sulphate and calcium nitrate treatments indicated their displacement by these treatments from shallower to deeper soil layers.

Fertilizer type effects. There was a greater NO_3-N concentration in the 0–5, 5–10, 10–15 and 90–120 cm layers resulting from ammonium sulphate application, and in the 15–30, 30–60 and 60–90 cm layers from calcium nitrate application compared to the other N fertilizers (Table 1). Urea treatments at both N rates had lesser NO_3-N concentrations in all soil layers as compared to the other N fertilizer treatments. Also, there was a maximum accumulation of NO_3-N concentration in the 15–30, 30–60, and 60–90 cm layers with nitrate (calcium nitrate), followed by nitrate-ammonium mixed (ammonium nitrate) and ammonium (urea and ammonium sulphate) fertilizers in decreasing order. With 336 kg N ha^{-1} for example, the NO_3-N concentration in the 30–60 cm layer was 384.0, 268.0, 112.8 and 30.5 mg kg^{-1} for calcium nitrate, ammonium nitrate, ammonium sulphate and urea, respectively. Similarly, the maximum increase in NO_3-N concentration due to a change in the N rate from 168 to 336 kg N ha^{-1} was 28.3, 107.0, 241.3 and 333.3 mg kg^{-1} for urea, ammonium sulphate, ammonium nitrate and calcium nitrate, respectively. These data show greater NO_3-N accumulation in the soil with nitrate-based than ammonium-based N fertilizers, especially at higher N rates. The lower NO_3-N concentration with urea than with the other ammonium-based fertilizer (ammonium sulphate) was probably due to higher ammonia volatilization losses to which urea is more susceptible when it is surface applied (Fen and Hossener 1985).

Greater NH_4-N concentration in the top 30 cm of the soil was observed with ammonium sulphate relative to the other fertilizers, except for the 15–30 cm layer at 168 kg N ha^{-1} (Table 1). On the other hand, mostly urea and sometime calcium nitrate showed a minimum NH_4-N concentration in the top 30 cm of the soil. The greater accumulation of NH_4-N with ammonium sulphate than with the other fertilizers was associated with its reduced nitrification due to lower soil pH (Malhi et al. 1991, 2000).

Significantly more extractable P was observed with ammonium sulphate than that with other N fertilizers in the 0–5 and 5–10 cm layers at both N application rates, and in the 10–15 and 15–30 cm layers at 336 kg N ha^{-1}. The concentration of extractable P in the top 15 cm of the soil was usually lower with urea and calcium nitrate than with ammonium nitrate or ammonium sulphate. The differences induced by the fertilizer type in the soil P concentration were attributed to the decrease in soil pH, i.e., higher P concentrations associated with a lower pH.

Unlike the concentration of NO_3-N, NH_4-N and P, the ammonium sulphate treatments had the lowest concentration of extractable Ca in the top 10 cm of the soil at both N rates, and in the 10-15 cm layer at 336 kg N ha^{-1}. At both N rates in the 0-5 cm and at 336 kg N ha^{-1} in the 5–10 cm layer, ammonium nitrate also reduced the Ca concentration compared to urea and calcium nitrate. The calcium nitrate resulted in significantly higher Ca concentration in the top 10 cm of the soil than the other fertilizers at both rates, in the 10–15 cm layer compared to ammonium nitrate and ammonium sulphate at 336 kg N ha^{-1}, and in the 15–30 cm layer relative to ammonium nitrate and urea at 336 kg N ha^{-1}. The application of ammonium sulphate at 336 kg N ha^{-1}, however, had a higher Ca concentration in the 15–30 cm layer compared to all other fertilizers and in the 30-60 cm layer compared to calcium nitrate and urea. A higher concentration of Ca in the shallow soil layers with calcium nitrate than with the other fertilizers was considered to be due to Ca additions associated with the calcium nitrate applications, while more accumulation of Ca in some deeper soil layers with ammonium sulphate was probably associated with soil acidity induced displacement and the subsequent downward movement of Ca from shallower to deeper soil layers.

The concentration of extractable Mg was the lowest with ammonium sulphate in the top 15 cm soil at both N rates and in the 15–30 cm layer at 336 kg N ha^{-1}. The concentration of Mg with urea was significantly higher and much greater than that detected in the calcium nitrate and ammonium sulphate treatments in the top 15 cm of the soil at both N rates, and in the 15–30 cm layer at 336 kg N ha^{-1}. Similarly, application of ammonium nitrate also tended to result in higher Mg

Table 2. Influence of 15 annual applications of 4 N sources at 2 rates on the concentration of macronutrients in bromegrass hay on a thin Black Chernozemic soil Crossfield, Alberta, Canada.

Rate of N	Source of N[a]	Concentration of macronutrients in hay						
		N	P	S	Ca	Mg	K	Ca/Mg ratio
(kg N ha^{-1})				(g kg^{-1})				
0	Check	10.6	1.0	1.40	3.5	1.24	12.7	2.82
168	AN	13.0	0.8	1.34	2.6	1.02	11.8	2.55
	Urea	12.2	0.8	1.35	3.0	1.10	12.1	2.73
	CN	14.7	0.9	1.56	3.2	1.16	12.7	2.76
	AS	14.2	0.9	2.59	3.1	0.95	13.1	3.26
336	AN	15.4	0.9	1.36	2.7	1.02	12.4	2.65
	Urea	13.6	0.8	1.30	2.9	1.10	12.5	2.64
	CN	14.9	0.8	1.44	2.9	1.03	13.3	2.82
	AS	15.7	0.8	2.29	2.9	0.89	11.8	3.26
$LSD_{0.05}$[b]		1.4	0.1	2.14	0.3	0.10	0.9	

[a]AN, CN and AS refer to ammonium nitrate, calcium nitrate and ammonium sulphate, respectively.
[b]The $LSD_{0.05}$ value is given when the F-test was significant and ns is given when the F-test was not significant.

concentrations in the top 15 cm of the soil than calcium nitrate and ammonium sulphate. In the 30–60 cm layer, however, ammonium sulphate and calcium nitrate showed a significantly higher Mg concentration than the other N treatments at 336 kg N ha^{-1}. This trend of lower concentration of Ca and Mg in the upper layers of soil and higher values in deeper layers indicated their greater downward movement by ammonium sulphate relative to the other fertilizers. Minimum K concentrations were usually observed with urea in the top 15 cm of the soil, while maximum levels of K concentration in the top 10 cm of the soil were observed with calcium nitrate at both rates of N application.

The changes in the concentration of the various macronutrients were often related to soil pH that were associated with the chemical form of N fertilizer being applied, as well as the addition of Ca contained in the calcium nitrate fertilizer.

Macronutrients in Bromegrass Hay

All the fertilizer treatments significantly increased the total N concentration in bromegrass hay (Table 2). A portion of the increase in N concentration due to N fertilization may have been from inorganic N, as NO_3-N has been observed to accumulate as a result of N fertilization by other researchers (Malhi et al. 1986, Penney et al. 1990). The concentration of total P, Ca and Mg (except for the case of Mg with calcium nitrate at 168 kg N ha^{-1}) were significantly reduced by all the N treatments. As expected, the concentration of total S in hay was significantly increased by the application of ammonium sulphate compared to the check treatment. None of the other fertilizers caused any noticeable change in the S concentration of the hay. The K concentration did not show any consistent effects of N addition. The decline of P, Ca and Mg concentrations due to N application was apparently the result of the dilution of these nutrients in greater amount of hay produced under fertilized conditions (Malhi et al. 1992). No change in the concentration of K was observed as a result of fertilizer N application. This suggests that there were sufficient K reserves present in soil for uptake by bromegrass hay at the elevated yields achieved in response to both of the N rates used in the study.

Increasing the ammonium nitrate, urea and ammonium sulfate rates from 168 kg N ha^{-1} to 336 kg N ha^{-1} significantly increased the total N concentration, but the increase for the calcium nitrate treatments was not significant. The concentration of the other elements was not consistently affected by the N rate.

Amongst the four N sources, the maximum total N concentration occurred with calcium nitrate at 168 kg N ha^{-1} and with ammonium sulphate at 336 kg N ha^{-1} whereas minimum values for total N concentration were observed with urea at both N rates. The concentration of total S in the hay was increased by the ammonium sulphate application, which resulted in significantly greater values than the other N fertilizer types. There was no consistent effect of fertilizer type on the P, Ca, Mg or K concentrations. The lack of differences in concentration of various macronutrients with source of N fertilizer was probably due to the fact that the level of N supply compared to the N requirements of bromegrass hay was more than enough at both rates of N application.

The Ca/Mg ratio was observed to increase with application of ammonium sulphate and to decline with application of ammonium nitrate, urea and calcium nitrate. Hypomagnesemia (grass tetany or staggers disease) may occur in animals fed on forage with Mg levels lower than 0.18 to 0.20% (Kemp et al. 1961, Grunes et al. 1970, Molloy 1971). Feeding high levels of Ca to animals increases Mg requirement or impairs Mg utilization (Nugara and Edwards 1961), which in turn can cause grass tetany in animals. In this experiment, Mg concentrations of all bromgrass hay samples were below normal, and application of N fertilizer further reduced the concentration of Mg in forage. The results of below normal Mg concentration and increase in Ca/Mg ratios in forage in some N fertilizer treatments in the present study suggest insufficient Mg in forage and the potential for tetany disease in animals.

Conclusions

The four N fertilizers (ammonium nitrate, urea, calcium nitrate and ammonium sulphate) applied annually for 15 years increased the concentrations of NO_3-N and NH_4-N but decreased the concentrations of extractable Ca, Mg and K in the surface soil. Increasing the N rate from 168 to 336 kg N ha^{-1} intensified the impact of the N effects on the concentration of macronutrients in soil for some of the treatments. In general, ammonium sulphate resulted in maximum changes and urea caused minimum changes in chemical soil properties. The nitrate-based fertilizers caused more accumulation of NO_3-N in the deeper soil layers than the ammonium-based fertilizers. In bromegrass hay, the total N concentration was increased due to the addition of N, but the concentration of other elements, except K, declined due to the dilution effect of the extra hay yield which resulted with the application of N fertilizer. Increasing the N rate from 168 to 336 kg N ha^{-1} further elevated the total N concentration in hay but had no effect on the concentration of other elements. The total N concentration in hay tended to be greater with ammonium sulphate, ammonium nitrate and calcium nitrate than urea.

In summary, the source and rate of N affected the concentrations of NO_3-N, NH_4-N, P, Ca, Mg and K in the soil but only the total N and S concentrations in bromegrass hay. Very high levels of NO_3-N in deeper soil layers, plus NO_3-N, NH_4-N and P in the shallower soil layers as a result of fertilizer N application clearly indicate a potential for environmental pollution problems to arise in similar situations.

References

Adams, S.N. 1984. Some effects of lime, nitrogen and soluble and insoluble phosphate on the yield and mineral composition of established grassland. J. Agr. Sci. Camb. 102: 219–226.

Campbell, C.A., A.J. Leyshon, H. Ukrainetz, and R.P. Zentner. 1986. Time of application and source of nitrogen fertilizer on yield, quality, nitrogen recovery and net returns for dryland forage grasses. Can. J. Plant Sci. 66:915–931.

Fen, L.B. and L.R. Hossener. 1985. Ammonia volatilization from ammonium and ammonium-forming nitrogen fertilizers. Adv. Soil Sci. 1:123–169.

Grunes, D.L., P.R. Stout, and J.R. Brownell. 1970. Grass tetany in ruminants. Adv. Agron. 22:331–374.

Hoyt, P.B. and A.M. Hennig. 1982. Soil acidification by fertilizers and longevity of lime applications in the Peace River region. Can. J. Soil Sci. 62:155–163.

Harapiak, J.T., S.S. Malhi, M. Nyborg, and N.A. Flore. 1992. Soil chemical properties after long-term nitrogen fertilization of bromegrass: Source and time of application. Commun. Soil. Sci. Plant Anal. 23:85–100.

Kemp, A., W.B. Deijs, O.J. Hemkes, and A.J.H. VanEs. 1961. Hypomagnesemia in milking cows: Intake and utilization of magnesium from herbage by lactating cows. Neth. J. Agric. Sci. 9:134–149.

Mahler, R.L. and R.W. Harder. 1984. The influence of tillage methods, cropping sequence, and N rates on the acidification of a northern Idaho soil. Soil Sci. 37:52–60.

Malhi, S.S., D.K. McBeath, and V.S. Baron. 1986. Effect of N application on yield and quality of bromegrass hay in central Alberta. Can. J. Plant Sci. 66:609–616.

Malhi, S.S., J.T. Harapiak, M. Nyborg, and N.A. Flore. 1991. Soil chemical properties after long-term N fertilization of bromegrass: nitrogen rate. Commun. Soil Sci. Plant Anal. 22:1447–1458.

Malhi, S.S., J.T. Harapiak, M. Nyborg, and N.A. Flore. 1992. Dry matter yield and N recovery from bromegrass in south-central Alberta as affected by time of application of urea and ammonium nitrate.. Commun. Soil Sci. Plant Anal. 23:953–964.

Malhi, S.S., J.T. Harapiak, M. Nyborg, and K.S. Gill. 2000. Effects of long-term applications of various nitrogen sources on chemical soil properties and composition of bromegrass hay. J. Plant Nutrition. 23:903–912.

Miller, J.R. and J.H. Axley. 1956. Correlation of chemical soil tests for available phosphorus with crop response, including a proposed method. Soil Sci. 82:117–127.

Molloy, L.F. 1971. Hypomagnesemic tetany and the chemistry of dietary calcium and magnesium. N.Z. Soil Bur. Rep. 5.

Nugara, D. and H.M. Edwards, Jr. 1961. Effect of calcium and phosphrus on magnesium metabolism in chicks. Fed. Proc., Fed. Am. Soc. Exp. Biol. 20: 294.

Penney, D.C., Malhi, S.S., and Kryzanowski, L. 1990. Effect of rate and sourceof N fertilizer on yield, quality and N recovery of bromegrass grown for hay. Fert. Res. 25: 159–166.

SAS Institute Inc. 1989. SAS/STAT Users Guide, Version 6, Fourth Edition, Volume 2 , SAS Institute Inc., Cary, NC, U.S.A. 846 pp.

Technicon Industrial Systems. 1973a. Ammonium in water and waste water. Industrial Method No. 90-70W. Revised January 1978. Technicon Industrial Systems, Tarrytown, NY, U.S.A.

Technicon Industrial Systems. 1973b. Nitrate and nitrite in water waste water. Industrial Method No. 100-70W-B. Revised January 1978 Technicon Industrial Systems, Tarrytown, NY, U.S.A.

Technicon Industrial Systems. 1977. Industrial/simultaneous determination of nitrogen and/or phosphorus in BD acid digests. Industrial Method No. 3334-74/Bt. Technical Industrial Systems, Tarrytown, NY, U.S.A.

Ukrainetz, H. and C.A. Campbell. 1988. N and P fertilization on bromegrass in the Dark Brown Soil zone of Saskatchewan. Can. J. Plant Sci. 68:457–470.