ACIDIFICATION OF A LUVISOLIC SOIL CAUSED BY LOW-RATE, LONG-TERM APPLICATIONS OF FERTILIZERS AND ITS EFFECTS ON GROWTH OF ALFALFA

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Soil samples collected from the Breton plots, which had received various treatments and had been cropped to a 5-yr rotation of cereals and forages over a 40-yr period, were analyzed to determine the effects of the treatments on soil acidity. Treatments included applications of fertilizers at low rates, infrequent applications of lime, applications of manure and applications of various combinations of these. Those receiving NS, NPS and NPKS were more acidic than the check plots and those receiving lime, lime + NPKS and P as 0–45–0 were less acidic. Plots treated with manure or manure + NPKS were not acidified. Since 1967, a brome–alfalfa mixture has been seeded and on the more acidic plots the established stand contained less than 30% alfalfa as compared to greater than 70% in the lime or P (0–45–0) treatments. Liming one half of each plot in each series in 1972 significantly increased the stand and reduced the aluminum content of alfalfa, especially in the more acidic plots. Alfalfa grown on these more acidic plots had, in general, higher Mn and Al and lower N contents than did alfalfa in the limed portions of the plots. The poor growth of alfalfa on plots receiving NS, NPS and NPKS is attributed to the acidifying effects of the fertilizers being sufficient to inhibit nitrogen fixation and induce some toxic concentrations of Al and Mn in the soil.

Des échantillons de sol ont été prélevés sur les parcelles Breton qui, au cours d'une période de 40 ans ont reçu divers traitements culturaux et ont suivi une rotation de 5 ans: céréales et cultures fourragères. On les a ensuite analysés pour mesurer les effets des traitements sur le degré d'acidité des sols. Les traitements comportaient des doses peu élevées de fumure chimique, des apports espacés de chaux, des épandages de fumier et diverses combinaisons de chacun de ces traitements. Les parcelles qui avaient reçu NS, NPS et NPKS avaient un degré d'acidité plus prononcé que les parcelles témoins, et celles traitées à la chaux seule ou avec NKPS ou à P (0–45–0) un degré moindre. Il n'y a pas eu d'acidification sur les parcelles recevant du fumier seul ou avec NPKS. Depuis 1967, la sole herbagère consiste en un mélange brome-luzerne. Sur les parcelles plus acides, le peuplement contenait moins de 30% de luzerne, contre plus de 70% dans les traitements chaux ou P. Le chaulage d'une moitié de chaque parcelle et de chaque série en 1972 a donné lieu à un accroissement de la proportion de luzerne dans le gazon établi et à une baisse de la teneur en aluminium de la luzerne, surtout dans les parcelles les plus acides au départ. En général, la luzerne cultivée sur la partie non chaulée des parcelles révélait de plus fortes teneurs en Mn et en Al et de plus faibles teneurs en N que dans les portions chaulées. La médiocre croissance de la luzerne dans les parcelles recevant NS, NPS et NPKS tiendrait aux effets acidifiants de ces engrais, effets assez forts pour inhiber la fixation azotée symbiotique et provoquer des accumulations toxiques de Al et Mn dans le sol.

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Fertility studies were begun on a Luvisolic (Gray Wooded) soil near Breton, Alberta in 1930. A rotation consisting of wheat, oats, barley (undersown to hay), 1st-yr hay and 2nd-yr hay, employing 11 treatments, was introduced in 1939. A detailed description of the soils and a history of the Breton plots has been given by Toogood et al. (1962) who indicate that fertilizers, especially those containing N, P and S have improved both yield and nutritive quality of the crops. During the period from 1939 to 1966, mixtures of various clovers and grasses were sown during the hay portion of the rotation. Since 1967, alfalfa (*Medicago sativa*) and brome (*Bromus inermis*) have been grown and it has been observed that plots which had received N and S fertilizers, excluding those which received these fertilizers in combination with lime and manure, and which had previously yielded the most hay were now producing the lowest yields. The poor performance of alfalfa in these plots was particularly apparent.

Fertilizers, especially nitrogen and sulfur compounds, applied at moderate to high rates frequently result in acidification (Voelcker 1874; Abruna et al. 1958; Adams and Pearson 1968; Toogood et al. 1975). However, the rates of fertilizer applied to the portion of the Breton plots discussed in this paper were much lower than most of the rates reported in the literature.

Fertilizers which contain nitrogen in the NH_4^+ form or which react to produce NH_4^+ in the soil are potentially more acidic than those containing NO_3^- (Hausenbuiller 1972). The addition of compounds such as KCl to a soil may result in exchange of Al and Fe species and H^+ from soil colloids and the former may undergo hydrolysis to provide acidic species (Coleman and Thomas 1967).

Pierre (1933) proposed a method for estimating potential acidity or basicity of fertilizers and, based on his estimate, commercial fertilizers had limestone or other basic materials included as an ingredient during the first few decades of fertilizer technology. However, in recent years, the trend has been to produce and use high-analysis sources of plant nutrients (Harre et al. 1971) most of which have an acidic reaction in the soil.

The sensitivity of alfalfa, and the even greater sensitivity of its symbiont to soil acidity is well documented in a comprehensive review by Robson (1969). Furthermore, alfalfa is known to have a high requirement for K, Ca and Mg and their use by the plant can be limited by soil acidity (Bear and Wallace 1950; Jones 1967).

The objectives of this study were to determine the acidification effects on a Luvisolic soil of nitrogen- and sulfur-containing fertilizers applied at low rates but over a long period of time, and to determine why these specific treatments had an adverse effect on the growth of alfalfa.

MATERIALS AND METHODS

The Breton plots are located 80 km southwest of Edmonton on a Gray Luvisol and Dark Gray Luvisol complex of soils (Toogood et al. 1975). Only fertilizer treatment plots 1–11 of series A, B, C, D and F involved in the 5-yr rotation were used in this study (Fig. 1). The fertilizer applications commenced in 1930 for series A–D and in 1939 for series F and have been applied at low rates on a regular basis ever since (Table 1).

Composite soil samples of the Ap horizon were obtained from plots 1 to 11 of series D in June 1971 and similarly from the west half (unlimed) of the 11 plots in series A, B, C and F

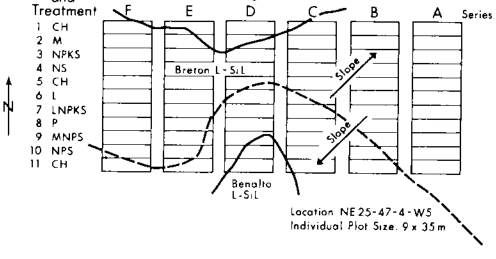

Fig. 1. Arrangement of fertilizer treatments and rotation series plus soil survey information for the Breton plots (see Table 1 for key to treatment symbols).

in June 1972. Sampling was confined to the west half of each plot because the east half of all plots was limed in 1972. The samples were air-dried and ground to pass through a 5-mm sieve.

Exchangeable cations were extracted using 1 N $NH_4C_2H_3O_2$ adjusted to *p*H 7.0. Ca, Mg, Na and K in the extract were determined by atomic absorption spectroscopy. Soil *p*H was determined using a 1:2 soil:water ratio (Peech 1965). Extractable Al and Mn (0.05 M $CaCl_2$) were determined by the procedure developed by Hoyt and Nyborg (1972). However, a 1-h shaking period followed by centrifuging at 3,500 rpm for 10 min, prior to filtration, was used and Al and Mn in the filtrate were determined by atomic absorption spectroscopy. Titratable acidity was determined using $BaCl_2$-Triethanolamine buffered at *p*H 8.0 (Peech 1965).

Plant samples for chemical analyses were taken on several occasions when the alfalfa was just commencing to bloom. In all but one case, only the terminal 15 cm of growth was sampled. The exception was for series A plots in 1972 when the whole plants were clipped about 2 cm above the ground because they were sampled during the establishment year and, at the time of sampling, were only about 15 cm tall. Samples of alfalfa and bulk forage were collected from series D plots in 1971 and from the unlimed half of plots in series F in 1972 when these series were in the "1st-yr-hay" part of the rotation. Samples of alfalfa were taken from the limed and unlimed halves of series A in 1972 when the series was in the "barley-undersown-to-hay" part of the rotation. Bulk forage samples for determining percent alfalfa in the stand were collected from the limed and unlimed halves of series A in 1973 when it was in the "1st-yr-hay" part of the rotation. All bulk samples were separated into alfalfa, clovers and grasses, and weeds, oven-dried at 60 C, and weighed; percent composition of each component was expressed on an oven-dry weight basis.

Alfalfa samples were oven-dried at 60 C and ground to pass through a 20-mesh sieve; nitrogen content was determined by the Kjeldahl-Wilford-Gunning method (Association of Official Agricultural Chemists (AOAC) 1955). The samples were dry-ashed (Isaac and Kerber 1971), treated with 2 M HCl, and filtered; Ca, Mg, Na, K, Fe, Mn and Al were determined by atomic absorption spectroscopy.

Table 1. Fertilizer, manure and lime treatments on plots 1–11 at Breton, 1965–1973†

		Nutrient kg/ha/yr			
Plot	Fertilizer	N	P	K	S
1 (CH)	Check plot	0	0	0	0
2 (M)	Manure‡	220	50	190	22
3 (NPKS)	16–20–0 0–0–60	11	6	16	9
4 (NS)	21–0–0 33.5–0–0	11	0	0	9
5 (CH)	Check plot	0	0	0	0
6 (L)	Lime§	0	0	0	0
7 (LNPKS)	Lime§// 16–20–0 0–0–60	11	6	16	9
8 (P)	0–45–0	0	6	0	0
9 (MNPS)	Manure‡	220	50	190	22
	16–20–0	11	6	0	9
10 (NPS)	16–20–0	11	6	0	9
11 (CH)	Check plot	0	0	0	0

†Prior to 1965, fertilizer was applied every 2nd yr to the appropriate treatments at the following rates (kg/ha) N-18, P-10, K-28, S-17.
‡Applied every 5 yr at 11 tonnes/ha. Nutrient rates shown above are annual equivalents.
§Lime (marl, slaked or hydrated) was broadcast and tilled into the soil seven times, between 1930 and 1948, at rates totalling 6.6, 5.4, 6.6, 7.8 and 6.6 tonnes/ha on series A, B, C, D and F, respectively. No lime was applied between 1949 and 1972, but the east half of all plots was limed to *p*H 6.5 in 1972.
//Prior to 1965, treatment was LP only.

Table 2. Percent alfalfa, clovers and grasses, and weeds in samples of 1st-yr hay from plots 1–11 of series A, D and F (dry weight basis)

Crop	1(CH)	2(M)	3(NPKS)	4(NS)	5(CH)	6(L)	7(LNPKS)	8(P)	9(MNPS)	10(NPS)	11(CH)
					Series A limed						
Alfalfa	81	NS†	72	79	95	NS	94	NS	27	72	76
Clovers & grasses	9	NS	24	18	2	NS	6	NS	63	26	13
Weeds	10	NS	4	3	3	NS	0	NS	10	2	11
					Series A unlimed						
Alfalfa	15	NS	2	6	76	NS	85	NS	20	5	41
Clovers & grasses	48	NS	93	88	20	NS	13	NS	67	90	54
Weeds	37	NS	5	6	4	NS	2	NS	13	5	5
					Series D						
Alfalfa	63	22	13	15	66	86	84	70	33	24	55
Clovers & grasses	31	65	46	37	20	13	11	23	48	32	32
Weeds	6	13	41	48	14	1	5	7	19	44	13
					Series F						
Alfalfa	46	26	20	19	41	86	84	80	32	29	51
Clovers & grasses	46	54	46	38	44	10	13	11	51	32	39
Weeds	8	20	34	43	15	4	3	9	17	39	10

†Not sampled.

RESULTS AND DISCUSSION

Low rates of fertilizer applied over a 40-yr period had a marked effect on certain soil properties (Figs. 2 and 3) and on the chemical composition and stand of alfalfa (Fig. 4 and Table 2). Statistical analysis reveals that a strong relationship exists between certain soil parameters and certain plant parameters (Table 3).

Before discussing the fertilizer-induced trends, it is important to indicate that a natural soil gradient occurs in two directions across the experimental area. Soil parameters *p*H, Ca/Σ [where Σ is the sum of exchangeable Ca, Mg, Na, K and titratable acidity (H)] and H/Σ for three check plots 1, 5 and 11 show that a gradient of decreasing acidity exists from the north end of the field to the south end (Fig. 2). For example, the average *p*H for plot 1 across all five series was 5.9 (north end) and the comparable value for plot 11 (south end) was 6.2. There is also a gradient of decreasing acidity across the field from east to west (series A to series F, Fig. 1) as illustrated by the same three parameters. The average *p*H value for the three check plots (1, 5, 11) in series A (east side) was 5.9 and the comparable average in series F (west side) was 6.3. However, there was essentially no gradient in the Σ values, which is a measure of cation exchange capacity. The three check plots (1, 5, 11) in series A (east side) had an average value of 21.5 meq/100 g of soil and the comparable value in series F (west side) was 21.9. Furthermore, the soil morphological characteristics were reasonably uniform over the experimental area because most of the treatment plots were located on the same soil type (Breton Si L, Fig. 1). The magnitude of the gradients is not considered excessive and is probably fairly typical of

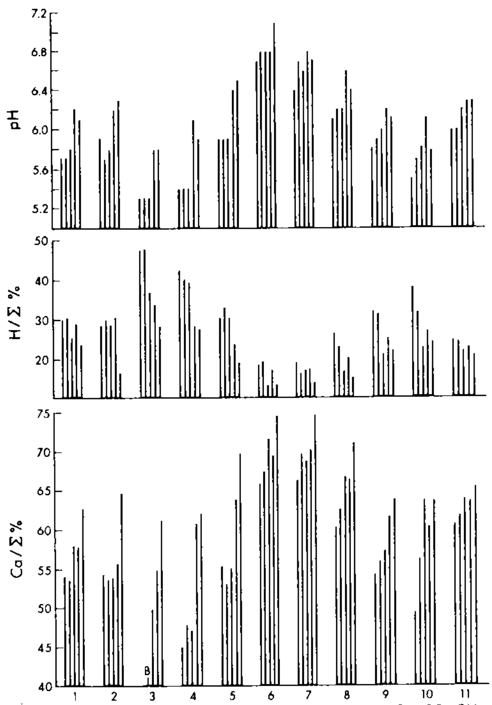

Fig. 2. Soil *p*H, H/Σ and Ca/Σ of Ap horizons for series A, B, C, D, and F, respectively, within each of the 11 treatment plots.

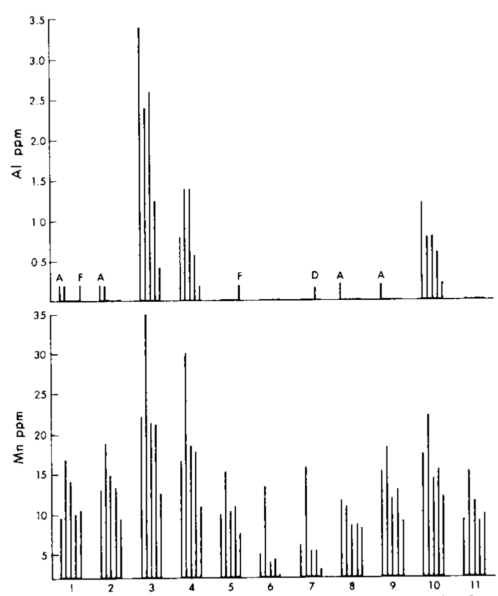

Fig. 3. Extractable soil Al and Mn of Ap horizons for series A, B, C, D and F, respectively, within each of the 11 treatment plots.

Luvisolic soils of the area. Since the Breton Si L soil at the plots was formed under deciduous–coniferous forest conditions, the gradient in the foregoing properties, which are related to soil acidity, was probably due to variability in forest cover during the weathering period since glaciation.

The acidification effects by certain treatments, although masked to some extent by the natural-acidity gradients, are clearly discernible. In general, *p*H and Ca/Σ are lower, whereas H/Σ, extractable Mn and Al are higher (Figs. 2 and 3) in plots 3 (NPKS),

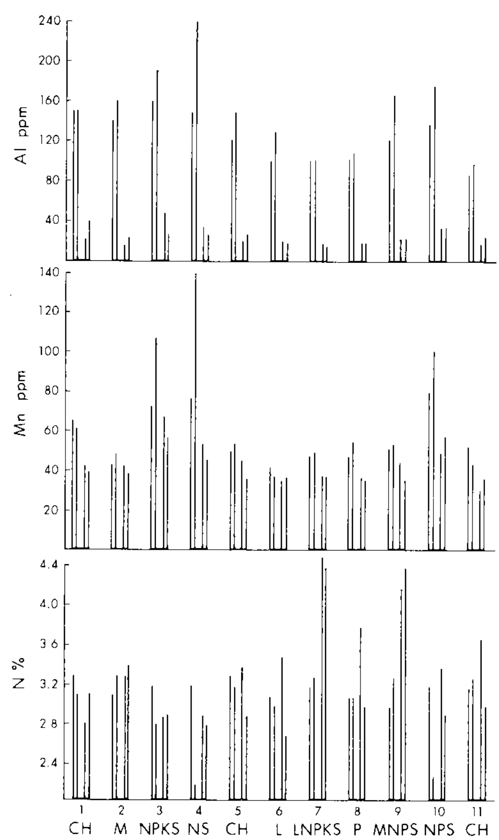

Fig. 4. Al, Mn and N contents of alfalfa sampled from series A (limed), A (unlimed), D and F, respectively, within each of the 11 treatment plots. Alfalfa was sampled from series A in the establishment year and from D and F in 1st-yr hay.

4 (NS) and 10 (NPS) than in the check plots, indicating that these treatments increased acidity. The reverse trends are apparent for plots 6 (L), 7 (LNPKS) and 8 (P, 0–45–0), indicating that these treatments decreased soil acidity. The acidification effects of the fertilizer treatments were greatest in series A and the following comparisons are made for this series to illustrate the treatment effects. In plot 3 (NPKS) the *p*H was 5.3 compared to an average *p*H of 5.8 for the nearby check plots 1 and 5, and the comparable values for H/Σ (hydrogen saturation) were 9.85 and 6.79%, respectively (Fig. 2). The comparable values for Ca/Σ (calcium saturation) were 40.1 and 54.8%, indicating that the fertilizer treatment lowered the calcium saturation considerably (Fig. 2). The extractable soil aluminum value for plot 3 was 3.4 ppm and the average for the two check plots (1 and 5) was only 0.1 ppm; the comparable extractable soil Mn values were 22.2 and 9.8 ppm, indicating very marked increases in extractable levels of these two elements as a result of the fertilizer applications (Fig. 3). A similar evaluation could be made for plots 4 (NS) and 10 (NPS) by comparing the various parameters in these plots to those in the nearest check plot. In each case, the trend is the same as that described for plot 3, although due to the natural gradient described earlier, plot 10 is not as acidic as plots 3 and 4. Also, the same trends for the various parameters exist within each of the other series as those discussed for series A, but again the effects diminish from series A to F due to the east–west gradient discussed earlier.

Plot 2 (M) and plot 9 (MNPS) received the heaviest application of nutrients of all the plots, but the soil in these plots was not as acidic as the soil in plots 3 and 4 that had received commercial fertilizer only. The practice at Breton has been to use well decomposed manure and to incorporate it immediately into the soil to minimize volatilization loss of nitrogen. It is apparent that nutrients applied as manure are not as

Table 3. Correlation of soil parameters with plant parameters for series A (unlimed), D and F

Soil parameters	Plant parameters		
	Mn	Al	% alfalfa in stand
(a) Series A (unlimed)†			
*p*H	−0.80**	−0.75**	0.89**
Ca/Σ	−0.84**	−0.84**	0.78*
H/Σ	0.88**	0.83**	−0.79*
Mn	0.77**	0.75**	−0.78*
Al	0.68*	0.50	−0.54
(b) Series D and F‡			
*p*H	−0.68**	−0.68**	0.86**
Ca/Σ	−0.62**	−0.52**	0.76**
H/Σ	0.72**	0.60**	−0.74**
Mn	0.78**	0.72**	−0.80**
Al	0.80**	0.79**	−0.55**

**Significant at $P \leq 0.01$.
*Significant at $P \leq 0.05$.
†All coefficients were computed on 11 pairs of data except for soil parameters vs. % alfalfa in stand, which were computed on eight pairs.
‡All coefficients were computed on 22 pairs of data.

acid-forming as those applied as commercial fertilizer and also indicates that the manure has served as an effective buffer against soil acidification.

Percent Alfalfa and Plant Nutrient Content

In series D and F, the *p*H, Ca/Σ, H/Σ, Mn and Al soil parameters, which are related to soil acidity, were each significantly correlated ($P \leq 0.01$) with plant Mn and Al contents and with percent alfalfa in the stand (Table 3). In series A, all the relationships except two were significant ($P \leq 0.01$ or 0.05). The fact that the correlations between soil and plant parameters are in most cases highly significant indicates that the soil parameter trends (Figs. 2 and 3) had an influence on plant contents of Mn and Al and percent alfalfa in the stand. The correlations between the soil parameters and percent alfalfa are particularly important because they indicate that the poor stand of alfalfa was related to soil acidity in the unlimed halves of plots 3 (NPKS), 4 (NS) and 10 (NPS) in series A, D and F (Table 2). The poor stand and vigor of alfalfa in these three treatment plots was the visual observation that prompted this study. Conversely, plots 6 (L), 7 (LNPKS) and 8 (P, 0-45-0) all contained greater than 70% alfalfa in the forage stand. The percent alfalfa in the check plots varied widely within and between series, but with only one exception (plot 1, series A, unlimed, Table 2) was it less than 40%. The data indicate that the soil in the check plots is borderline for alfalfa production and low rates of N,S fertilizers applied over a long period of time were sufficient to acidify the soil enough to adversely affect alfalfa production. However, when the soil was limed and fertilized, alfalfa grew well. Liming the east half of series A resulted in a marked increase in plant vigor (Webster and McCoy 1974) and significantly decreased the aluminum content of alfalfa (paired t-test, $P \leq 0.01$).

Although Mn and Al contents of alfalfa (series D and F) are significantly correlated with soil acidity (Table 3), the concentrations (Fig. 4) do not approach those suggested by Jones (1967) as being excessive (100 ppm Mn, 200 ppm Al) for similarly sampled plants. In contrast, alfalfa plants from the unlimed halves of plots 3, 4 and 10 in series A had Mn contents greater than 100 ppm and those from plot 4 had an Al content of 240 ppm, suggesting that toxic levels may have existed. However, the portion of plants used for this determination (entire plant, cut 2 cm above ground) was different than that on which Jones based his critical values. Al and Mn contents of alfalfa plants from Series A (limed and unlimed) were significantly higher (unpaired t-test $P \leq 0.01$) than those from series D and F (Fig. 4). This may have been partially due to series A being more acidic than the other two, but probably was primarily due to the difference in the part of the plant sampled and the difference in physiological stage of growth at time of sampling.

Based on extensive experience, M. Nyborg (Professor of Soil Science, University of Alberta, personal communication) regards $CaCl_2$-extractable soil Al of 1.5 ppm and Mn of 20 ppm as the levels above which considerable growth damage is likely to occur on alfalfa. Based on these values, plot 3 of series A, B and C had toxic levels of Al (Fig. 4) and plot 4 of series B and C and plot 10 of series A had borderline levels. For Mn, plot 3 in series A, B, C and D and plots 4 and 10 in series B exceeded the 20 ppm level. The foregoing comparisons suggest that Al and Mn toxicities were probably partially responsible for the poor performance of alfalfa in these more acidic plots.

The N contents of alfalfa plants grown on series D and F (Fig. 4) were less than 4% on all treatments except plot 7 (LNPKS) and plot 9 (MNPKS). Similarly sampled alfalfa with less than 4% N is regarded by Jones (1967) as being critically low. There are major differences evident in the nitrogen content of plants grown on the limed half of series A compared to their unlimed counterparts. The major increase in nitrogen content due to liming occurred on plots 3 (NPKS), 4 (NS) and 10 (NPS) (Fig. 4). The low nitrogen content of plants in these more acidic plots indicates that nitrogen fixation was inhibited and the low rates of nitrogen applied were not sufficient to supply plant requirements. Although there is also the possibility that growth was inhibited by Al and Mn as discussed earlier, Munns (1965) suggests that in moderately acidic soils (*p*H 5.5–6.0), growth reductions of alfalfa were due to restricted activity of *Rhizobia*. It should be noted that plots 3 and 4 for series A, B, and C had *p*H values in the 5.0–5.5 range, which is lower than that reported by Munns. Supporting the low nitrogen fixation concept is the observation that in a greenhouse experiment when soils from plot 3 (NPKS) series C and D were supplied with 50 ppm N (McCoy 1973 unpublished), alfalfa grew well compared to that grown in the unfertilized soil. It would appear that the poor growth of alfalfa in the more acidic plots was due to a combination of poor fixation of nitrogen plus some toxic effects of Al and Mn.

CONCLUSION

Relatively small amounts of fertilizer N and S applied over a 40-yr period to a Luvisol at Breton have resulted in an increase in soil acidity sufficient to reduce alfalfa production. Infrequent applications of small amounts of lime prevented these developments.

Luvisolic soils presently comprise approximately 15% of the cultivated acreage in Alberta, but it is estimated that in future they may comprise up to 40% of the total (Bentley et al. 1971). Many of these soils are deficient in nitrogen and sulfur and these nutrients must be applied, but applications of such fertilizers may result in acidification. The results of this study suggest that the adoption of a practice of liming these soils should be introduced as soon as feasible. Such a practice is not common, although recent work (Hoyt et al. 1967; Penney 1973) has clearly demonstrated its advisability.

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