CHANGES IN SOIL CHEMICAL PROPERTIES DUE TO 40 YEARS OF FERTILIZATION

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Continuous fertilization for 40 years with N and P resulted in significant changes in soil pH, lime requirement, organic matter, Bray and Kurtz no. 1 P, and DTPA-extractable micronutrients. A pasture soil receiving up to 224 kg N ha⁻¹ as ammonium nitrate and 45 kg P ha⁻¹ as superphosphate since 1946 was analyzed for soil test values as a function of depth. Soil pH values were observed to decrease when N applications exceeded plant requirements. In plots receiving continuous additions of 224 kg ha⁻¹, the pH decreased from 6.5 to 4.1. The lime requirement of the soils reflected pH changes. Organic matter was found to be unaffected by P fertilization, but increased with increasing N rate. Bray and Kurtz no. 1 P concentrations were extremely high in the surface 10 cm of P-fertilized plots, and increased concentrations were observed to a depth of 60 cm. DTPA-extractable Fe was negatively correlated with pH, and increased DTPA-Fe was observed to a depth of 20 cm. DTPA-Mn also tended to increase in soils with lower pH, and both total and DTPA-extractable Mn appeared to have leached from the 0- to 10-cm to the 10- to 20-cm increment in soils receiving the highest rate of N application. A strong interaction of N, P, and depth was observed for DTPA-Zn, but DTPA-Cu was unaffected by fertilization. In 1965, the plots were split, with one-half of each plot continuing to receive fertilizer and the other half having the fertilization permanently discontinued. The soil pH, lime requirement, Bray and Kurtz no. 1 P, and DTPA-extractable Fe and Mn all showed a significant response to discontinuation of fertilizer additions. The pH tended to increase, whereas the lime requirement, Bray and Kurtz no. 1 P, and DTPA micronutrients decreased during the 20 yr without fertilizer.

Nitrogen-containing fertilizers are often applied to maintain pasture crops, but continued use of ammonia-based fertilizers can induce soil acidity. Pierre (1928) published a classic study quantifying the acidifying effects of ammonia-based fertilizer and indicating that oxidation of NH₄⁺ to NO₃⁻ (nitrification) produces two moles of H⁺ per mole of NH₄⁺. Abruna et al. (1958) applied very high rates of N (up to 1200 kg ha⁻¹·yr⁻¹) for 3 yr and observed a change from pH 7 to 3.9 in the surface soil (0 to 15 cm) and significant changes in pH at depths of 45 cm. Similar data were obtained by Wolcott et al. (1965), using 330 kg NH₄-N ha⁻¹ for 5 yr. In no-till or permanent pasture conditions, the surface application of ammonia-based fertilizer can severely reduce the pH of the surface soil (Westerman 1981; Mahler and Harder 1984), even when moderate N applications are used (Berg 1986; Smika et al. 1961).

Long-term application of P fertilizer most often results in increased plant-available P at the depth of application, with no downward migration of P (Spencer and Stewart 1934; Brown 1935; Hannapel et al. 1964; Rechcigl et al. 1985). However, leaching of inorganic P has been observed by some researchers to depths of 10 cm (Heck 1934), 20 cm (Brown 1935), and 60 cm (Stephenson and Chapman 1931). Wagar et al. (1986) observed increases in HCO₃⁻ extractable P at depths of 15 to 30 and 30 to 60 cm after 5 yr of application of up to 80 kg P ha⁻¹ on Canadian soils under cereal cropping. Long-term fertilization with N was found to increase bicarbonate-extractable P relative to unfertilized plots (Rogler and Lorenz 1969; Smika et al. 1961).

Little information is available concerning the effects of long-term fertilization on micronutrient soil-test values, but the effects of P on micronutrient solubility and availability to plants have been studied. The equilibrium solubility of Zn decreases as pH increases (Lindsay 1979), and measured solubilities support this general trend (Lindsay and Norvell 1969; Bar-Yosef 1979; Shuman 1975; Cavallero and Mc-

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Bride 1984; Saeed and Fox 1977). Similarly, the solubilities of Fe (Norvell and Lindsay 1982), Cu (Cavallerio and McBride 1984), and Mn (Sims 1986) decreased with increasing pH.

Owensby et al. (1969) reported changes in pH, lime requirement, and available P after 20 yr of fertilization. Significant depression of pH was observed to a depth of 15 cm, and soil-test P increased to a depth of 45 cm. Those experimental plots were split in 1965, with half of each plot continuing to receive annual fertilizer additions, and fertilization being discontinued in the other half. Splitting the plots this way would allow future investigations into the effect of continued fertilization as well as the recovery from the first 20 yr of fertilizer additions.

The objectives of this research were to (1) quantify the effects of 40 yr of fertilization with ammonium nitrate and superphosphate on soil-test values of a soil growing continuous smooth brome (Bromus inermis Leyss); (2) determine the depth to which soil test values were affected; and (3) observe the changes when fertilizer was applied for 20 yr and then discontinued for 20 yr.

MATERIALS AND METHODS

Plot history and design

The plot area was located on the Kansas State University Agronomy Farm near Manhattan, Kansas. Initial fertilizer application was in 1946 on an 8-yr-old stand of Achenbach smooth brome. Prior to establishment of the smooth brome, the area had been in native True Prairie vegetation and never plowed. The plot area was mapped a Smolan silt loam, 3 to 8% slopes (fine, montmorillonitic, mesic Pachic Argiustolls).

Individual plots were 3 × 6 m. Nitrogen treatments were 0, 22, 67, 112, 157, and 224 kg·ha⁻¹ applied in early March each year as ammonium nitrate. Phosphorus treatments were 0 and 45 kg·ha⁻¹ applied as superphosphate in early March each year. Experimental design was a two-replicate split-split-split plot with phosphorus rate as the main plots and nitrogen rate as subplots, discontinued versus continued application as subplots, and depth as subsubplots.

Soil sampling, preparation, and analysis

Soils were sampled during the summer of 1985. Each plot was sampled in duplicate using a 5-cm stainless steel tube driven by a hydraulic press. Cores were removed from the tube, and the outside of the core was removed to prevent contamination. The cores were divided into increments of depth and air-dried. The samples then were ground to pass a 2-mm sieve and stored in airtight plastic containers.

The soils were analyzed by the Kansas State University Soil Testing Laboratory using standard procedures (Dahake 1980). Soil pH was determined on a 1:1 soil-water suspension. Lime requirement was determined using the SMP buffer (Shoemaker et al. 1961). Extractable P was determined using the method of Bray and Kurtz (1945) and analyzed by the ascorbic acid modification of the molybdate-blue method (Watanabe and Olsen 1965). Organic matter was determined using the method of Walkley and Black (1934) modified for colorimetry (Graham 1948). Zinc, Fe, Cu, and Mn were extracted using the DTPA soil test (Lindsay and Norvell 1978) and analyzed by atomic absorption spectrometry.

Statistical analyses

The soil chemical data were analyzed as a split-split-split plot with the main plots being rates of P, and the splits being rates of N, discontinued versus continued, and depth using SAS-ANOVA (SAS Institute, Cary, North Carolina). Mean separation was by Duncan's LSD (P < 0.05).

RESULTS AND DISCUSSION

To provide a point of reference, selected chemical and physical properties are given in Table 1. Changes induced by fertilization are discussed below.

<table>
<thead>
<tr>
<th>Depth, cm</th>
<th>CEC, cmol kg⁻¹</th>
<th>Sand, %</th>
<th>Silt, %</th>
<th>Clay, %</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–10</td>
<td>20.1</td>
<td>8</td>
<td>58</td>
<td>34</td>
<td>6.5</td>
</tr>
<tr>
<td>10–20</td>
<td>20.2</td>
<td>8</td>
<td>61</td>
<td>31</td>
<td>6.1</td>
</tr>
<tr>
<td>20–30</td>
<td>19.8</td>
<td>8</td>
<td>53</td>
<td>39</td>
<td>5.9</td>
</tr>
<tr>
<td>30–45</td>
<td>19.4</td>
<td>8</td>
<td>56</td>
<td>36</td>
<td>6.0</td>
</tr>
<tr>
<td>45–60</td>
<td>19.1</td>
<td>8</td>
<td>53</td>
<td>39</td>
<td>6.1</td>
</tr>
<tr>
<td>180–240</td>
<td>17.7</td>
<td>19</td>
<td>55</td>
<td>26</td>
<td>6.7</td>
</tr>
<tr>
<td>300–360</td>
<td>14.8</td>
<td>25</td>
<td>63</td>
<td>12</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Dry matter yield

The yield of smooth brome from the plots was not affected by P fertilization, but was strongly influenced by rate of N application (data not shown). Yield increased significantly relative to the control for all rates, but maximum yield was realized at 67 kg N·ha\(^{-1}\). Further increases in the rate of N did not change the yield. This was in agreement with the soil test recommendation for the 0 kg N rate of 67 kg N·ha\(^{-1}\). Therefore, rates exceeding this are considered excessive.

pH and lime requirement

Phosphorus fertilization did not affect the pH or lime requirement of the soils. The pH was strongly affected by the rate of nitrogen application (Fig. 1A), especially when the rate of fertilization exceeded 67 kg N·ha\(^{-1}\). For the 0- to 10-cm increment, the pH ranged from 6.2 to 6.6 for the 0-, 22-, and 67-kg N·ha\(^{-1}\) treatments, but the pH decreased to 5.5 for the 112 and 157 rates and to 4.1 for the 224-kg N·ha\(^{-1}\) rate. Soil pH decreased with increasing N for the 10- to 20-cm increment, but not for greater depths.

Significant declines in pH were observed only in the soils receiving excessive ammonium. However, even low rates of N application resulted in significant pH suppression, in agreement with Berg (1986). Because the fertilizer was applied in the spring when the brome was active and growing, the N was readily used unless the fertilization rate was above the plant requirement. Uptake of N helps reduce nitrification and, thus, acidification of the soil (Jolley and Pierre 1977). The pH of soils receiving no fertilizer from 1965 to present (Fig. 1B) still reflected the acidifying influence of the ammonium, but the effects were less than those for the soils receiving continuous fertilization (Fig. 1A). Recovery in pH of these soils during the 20 yr without N can be demonstrated by comparing the 1985 values to those reported by Owensby et al. (1969). The 1985 pH values show an apparent increase relative to 1965, but the statistical significance could not be determined because of differences in sampling depths and changes in instrumentation. However, it appears that the pH has increased in the 112-, 157-, and 224-kg N treatments compared with 1965, with no change in the 0-, 22-, and 67-kg N·ha\(^{-1}\) treatments. In 1965, the 224-kg N treatments had mean pH values of 4.7 for the surface soils (0 to 15 cm) compared to 4.2 for the continuously fertilized plots in 1985 and 5.8 for the plots in which fertilization ceased. The pH of the continuously fertilized plots continued to decrease, while the discontinued plots showed a recovery of 1.1 pH units. The pH depression with high rates of N fertilization was significant only in the surface in 1965, possibly because of depth of sampling (15-cm increments).

The pH increases in the discontinued treatments resulted from the removal of acidity by one or a combination of the following mechanisms: (1) slow precipitation/dissolution of oxide minerals in the soil (such as iron, aluminum, or aluminosilicates) effectively neutralized the excess acidity; (2) base cycling by the brome resulted in the translocation of Ca, Mg, and K from the subsoil to the surface layers. So, increased bases relative to acidity result in higher pH; (3) the acidity was leached from the surface layers and distributed at greater depth; and (4)

![Fig. 1. The effect of N fertilization on pH, averaged over P rates. A, continuously fertilized plots. B, plots in which fertilization was discontinued in 1965. The least significant difference (lds, P < 0.05) between N rates for a given depth and either continued or discontinued fertilization was 0.33; lsd comparing continuous versus discontinued fertilization at a given depth and N rate was 0.31.](image-url)
deposition of basic materials on the soil surface neutralized the acidity. The disappearance of exchangeable Al from the most acidic soils (Schwab et al. 1989) and the increase of exchangeable Ca, Mg, and K support mechanisms 1, 2, and 4. The possibility of surface deposition of basic materials is supported by the proximity of a limestone-graveled road. The closest plots were within 10 m of the road, and of those even the continuously fertilized plots showed an effect of the limestone dust in surface layers. The majority of the plots at greater distance showed little or no effect.

Lime requirements as predicted by the SMP buffer (Table 2) followed the same trends as pH. Lime requirement was near 0 for the 0-kg N·ha⁻¹ treatments and increased steadily with increasing N rates. Lime requirement changes significantly with depth for the highest rates of N. When the data for the 224-kg N treatment were compared, lime requirements were higher in 1965 (15 500 kg·ha⁻¹) than those of the continuous (12 500 kg·ha⁻¹) and the discontinued plots (3500 kg·ha⁻¹) in 1985. The soils seemed to be able to partially recover from the fertilizer-induced acidity during the 20 yr without fertilization.

**TABLE 2**

Mean values of lime requirement and organic matter as affected by rate of N application, depth, and discontinuation of fertilization averaged over P rates

<table>
<thead>
<tr>
<th>Depth, cm</th>
<th>Lime requirement</th>
<th>Organic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/ha</td>
<td>g/kg</td>
</tr>
<tr>
<td>Continuous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10</td>
<td>0 1310 4870 12500 38 45 47 48</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>10-20</td>
<td>2920 2090 2640 3930 34 38 36 35</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>20-30</td>
<td>1790 2750 3560 4620 31 33 31 31</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>30-45</td>
<td>2190 2670 2810 2120 24 27 26 26</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>45-60</td>
<td>2250 2120 2370 2180 16 20 18 19</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>Discontinued</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10</td>
<td>0 180 1500 3120 42 42 44 41</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>10-20</td>
<td>1250 1750 3870 5430 38 37 37 35</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>20-30</td>
<td>1790 2180 3560 4310 32 32 32 32</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>30-45</td>
<td>2310 2610 2630 3370 26 26 26 26</td>
<td>0 67 157 224</td>
</tr>
<tr>
<td>45-60</td>
<td>2690 2500 2280 2580 17 18 19 17</td>
<td>0 67 157 224</td>
</tr>
</tbody>
</table>

Discontinued (N rate)¹

| 1sd (N rate)¹ | 2100 | 4 |
| 1sd (depth)² | 2600 | 3 |
| 1sd (disc.)³ | 2900 | 3 |

¹ Least significant difference (P < 0.05) due to N rate.
² Least significant difference (P < 0.05) due to depth.
³ Least significant difference (P < 0.05) due to discontinuation of fertilization.

**FIG. 2.** The effect of P fertilization on Bray P as a function of depth. The least significant difference (1sd, P < 0.05) between 0 and 45 kg P/ha at any given depth was 1.2 on the data transformed by natural logarithm (top axis); 1sd between continuous and discontinued fertilization at any given depth was 0.4 on the transformed data.

**Organic matter**

The organic matter contents of the soils did not respond to P fertilization, but they did respond to N (Table 2). Organic matter was lowest at the lowest N rate (averaged over P rates), and this mean content was significantly different from those of all other N rates. As expected, the organic matter declined with increasing depth.

**Phosphorus**

Although unfertilized brome in the experimental plots showed P deficiency, the continuous, annual addition of 45 kg P·ha⁻¹ exceeded the plant requirement for P. As a result, soil test P built up to concentrations of 150 to 225 mg P·kg⁻¹ soil at the surface, whereas the plots without P application averaged less than 10 mg P·kg⁻¹ (Fig. 2). The most notable aspect of the Bray and Kurtz no. 1 P concentrations was the depth to which increases were observed. After the data were transformed using natural logarithms to compensate for the variability in the concentration in the 0- to 10-cm increment of the fertilized plots, significant differences between fertilized and unfertilized plots were ob-
served to a depth of 60 cm. That was a remarkable depth of penetration of the P, considering that the inorganic P was applied to the surface with no incorporation. The mechanism of movement of the P is not clear, but could be the result of one or more of three possible means of transport: (1) the P could simply be leached as the inorganic orthophosphate. High amounts of rainfall often occur shortly after fertilization when the solubility of the superphosphate is still high. This mechanism is supported by the observation that Bray and Kurtz no. 1 P and \( \text{H}_2\text{PO}_4^- \) activities were highly correlated to a depth of 60 cm in the fertilized plots (Schwab and Kulyingyong 1989). (2) The P may be transported as organic phosphates after initial immobilization. Organic phosphates are known to be more mobile than the inorganic (Heck 1934; Stephenson and Chapman 1951; Hannapel et al. 1964) and subsequent mineralization after translocation could explain the previously observed elevated \( \text{H}_2\text{PO}_4^- \) activities with depth. (3) The P may be transported through plant roots with subsequent exudation of P and/or P remaining after the roots die. Wagat et al. (1986) found that both organic and inorganic forms of P are mobile in some soils, but the mechanism of transport in our system is unresolved.

**Iron**

Although there was not a significant effect of P fertilization on DTPA-extractable Fe, there was a strong effect of N fertilization and depth (Fig. 3). In the absence of applied N, DTPA-Fe was approximately 50 mg·kg\(^{-1}\) for the 0- to 10-, 10- to 20-, and 20- to 30-cm depths. The first significant increase in DTPA-Fe in the continuously fertilized plots occurred in the 0- to 10-cm increment for the 112-kg N·ha\(^{-1}\) treatment with a concentration of 73 mg·kg\(^{-1}\) (Fig. 3A). Concentrations of 110 and 130 mg·kg\(^{-1}\) were observed for the 157- and 224-kg N·ha\(^{-1}\) treatments, respectively. Concentrations were lower in the 10- to 20-cm increment for the 112-, 157-, and 224-kg N·ha\(^{-1}\) treatments, but were still higher than those with the lower rates of N. There were no significant differences between treatments for depths greater than 20 cm.

In the plots in which fertilizer was discontinued in 1965 (Fig. 3B), the trends were similar to those in the continuously fertilized plots, except the concentrations were lower. A maximum of 95 mg Fe·kg\(^{-1}\) was observed in the 0- to 10-cm increment that had received 224 kg N·ha\(^{-1}\). This concentration was significantly greater than the DTPA-Fe in the 157- and 112-kg N·ha\(^{-1}\) plots. The 0- and 22-kg N·ha\(^{-1}\) plots had the lowest concentrations of approximately 40 mg Fe·kg\(^{-1}\).

Differences due to N fertilization were still observed in the 10- to 20-cm increment, but disappeared in the 20- to 30-cm depth.

The effects of N fertilization on DTPA-Fe were predictable, knowing the effects of N on pH. One would expect that the solubility and extractability of Fe would increase as pH decreased due to the long-term fertilization with ammonium. It was observed that as pH decreased, DTPA-Fe increased for both the continuously fertilized plots and the plots in which fertilization was discontinued. The strength of the relationship between pH and DTPA-Fe was tested by running regression analyses (Table 3).
TABLE 3
Slopes (with 95% confidence intervals) and correlation coefficients ($r^2$) for regression analyses of DTPA-Fe and DTPA-Mn versus pH

<table>
<thead>
<tr>
<th>Element</th>
<th>Depth, cm</th>
<th>Slope</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0-10</td>
<td>-43 ± 4</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>10-20</td>
<td>-27 ± 5</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>-13 ± 5</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>-29 ± 4</td>
<td>0.55</td>
</tr>
<tr>
<td>Mn</td>
<td>0-10</td>
<td>-5 ± 4</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>10-20</td>
<td>-17 ± 5</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>-15 ± 6</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>-9 ± 3</td>
<td>0.23</td>
</tr>
</tbody>
</table>

For the first depth, the slope was negative (-43) with $r^2 = 0.89$. In the 10- to 20-cm depth, the slope was again negative (-27), with a high correlation coefficient of $r^2 = 0.70$. As the sampling depth increased, the range in concentrations decreased, and the correlations became weaker. In the 30- to 45- and 45- to 60-cm depths, where there was no observed effect of N fertilization, the $r^2$ values were nearly zero. These data are consistent with the results of Shuman (1986), who found that DTPA-Fe was positively correlated with exchangeable and organically bound Fe, which, in turn, was strongly negatively correlated with pH.

Manganese

The effect of N fertilization on DTPA-Mn was similar to the effect on DTPA-Fe (Fig. 4). In the top two depths, concentrations were higher in the plots receiving higher rates of N because of the depression of pH. The effects were significant to a depth of 20 to 30 cm. There was a notable difference in the pattern of DTPA-Mn compared with DTPA-Fe in the 224-kg N·ha$^{-1}$ plots of both the continuous and discontinued treatments. The DTPA-Mn was lower in the 0- to 10-cm increment than in the 10- to 20-cm. In fact, the DTPA-Mn in the 0- to 10-cm increment of the continuous 224-kg N plot was one of the lowest concentrations observed, and the concentration in the 10- to 20-cm increment was the highest. Possibly, the Mn leached from the upper increment of soil in the low pH environment and accumulated in the 10- to 20-cm increment where the pH was higher. This theory was tested by measuring the total Mn the 0- to 10- and the 10- to 20-cm increments of the 0- and 224-kg N·ha$^{-1}$ treatments. The results indicated that the changes in DTPA-Mn were accompanied by decreased total Mn. The 0-kg N treatments contained a total of 430 ± 25 mg·kg$^{-1}$ soil and 16 mg DTPA-Mn·kg$^{-1}$ in both the 0- and 10-cm increments. In the individual 224-kg treatments, total Mn was strongly correlated with DTPA-Mn ($r^2 = 0.72$). The lowest total Mn contents (240 mg·kg$^{-1}$) were observed in the surface 10 cm and were associated with the lowest DTPA-Mn (8 mg·kg$^{-1}$). The highest totals (610 mg·kg$^{-1}$) were found in the 10- to 20-cm layers, as were the highest DTPA-extractable concentrations (81 mg·kg$^{-1}$). Apparently, the very low pH values in the surface 10 cm of soil of the 224-kg treatments increased the mobility of the more soluble fractions of Mn. The solubilized Mn was leached, leaving less soluble forms of Mn, and was reprecipitated in the 10- to 20-cm layer in a form readily extractable by DTPA.

**FIG. 4.** The effect of fertilization on DTPA-extractable Mn as a function of depth. A, continuously fertilized plots. B, plots in which fertilization was discontinued in 1985. Least significant difference (LSD, $P < 0.05$) between N rates at any given depth and either continued or discontinued fertilization was 11; LSD comparing continuous versus discontinued fertilization at a given depth and N rate was 15.
The correlation between pH and DTPA-Mn (Table 3) was poor at all depths ($r^2 = 0.11$ to 0.48) because of the low DTPA-Mn in the surface soil at low pH. The correlation improved ($r^2 = 0.60$) if the 224-kg N·ha$^{-1}$ plots were removed from the analysis. The weak relationship between DTPA-Mn and pH was in partial agreement with the data of Shuman (1986). In that study, DTPA-Mn was positively correlated with exchangeable Mn and Mn associated with crystalline Fe oxides, but neither was correlated with pH.

**Zinc**

DTPA-extractable zinc was affected by N, P, depth, and discontinuation of fertilization, and a significant, four-way interaction was observed among these factors. As a result, we will discuss the effects of N rate at a given depth, P rate, and continuous/discontinuous treatment on DTPA-Zn (Fig. 5). Extractable Zn in the continuously fertilized plots with 0 P (Fig. 5B) showed no significant effect of N rate at 112 kg N·ha$^{-1}$ and below. At the 157-kg rate, DTPA-Zn in the surface increment was greater than at the 0 rate, but DTPA-Zn for the 224-kg rate was significantly less than for the 0-kg N rate. The same trend was observed in the 10- to 20-cm depth, but the differences were not significant. Significant decreases in DTPA-Zn to a depth of 20 to 30 cm for N rates greater than 67 kg N·ha$^{-1}$ were observed in the plots with continuous applications of 45 kg P·ha$^{-1}$.

DTPA-Zn was plotted as a function of pH for the continuously fertilized plots in an attempt to explain this unexpected result (Fig. 6). There was little relationship between pH and DTPA-Zn for the 0-P treatments (Fig. 6A), but the effect of depth was evident in the amount of Zn extracted. For the 45-kg P·ha$^{-1}$ treatments (Fig.

**Fig. 5.** The effect of fertilization on DTPA-extractable Zn as a function of depth. A, 45 kg P/ha, continuous fertilization. B, 0 kg P/ha, continuous fertilization. C, 45 kg P/ha, discontinued fertilization. D, 0 kg P/ha, discontinued fertilization. Least significant difference (lSD, $P < 0.05$) due to P fertilization at any given N rate, depth, and either continued or discontinued fertilization was 1.1; lSD comparing N rates for a given depth and either continued or discontinued fertilization was 0.4; lSD comparing continuous versus discontinued fertilization at a given depth and N rate was 0.4.
There was a strong relationship between pH and DTPA-Zn; concentration increased with increasing pH. If DTPA-Zn was controlled by dissolution of Zn minerals (Lindsay 1979) or exchangeable Zn (Shuman 1986), then the slope of the lines in Fig. 6B should have been negative, not positive. Therefore, it seems that the interaction between pH, P, and DTPA-Zn was related to the chemistry of the extracting solution rather than the soil chemistry of Zn. Research is currently under way to investigate the relationship between uptake of Zn by smooth brome in these plots and DTPA-Zn.

Copper

There was no effect of fertilization with either N or P on DTPA-Cu. Extractable Cu did increase significantly with depth, as shown in Table 4. That trend is opposite those of the other three DTPA-extractable elements measured in this study. Because organic matter decreased with depth in these soils, a decrease in DTPA-extractable concentration with depth would suggest an interaction of the element with organic matter. However, Shuman (1986) found a positive correlation between organically bound and DTPA-extractable Fe and Cu and a negative correlation between organic matter and DTPA-Zn and Mn. Based only upon total organic matter, our results would appear to disagree with those data for Cu, Mn, and Zn, but this cannot be resolved without actually measuring the organically bound micronutrients in our soils.

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