Relationship of Ammonium Nitrogen Distribution to Mineralogy in a Hapludalf Soil

D. L. Sparks, R. L. Blevins, H. H. Bailey, and R. I. Barnhisel

ABSTRACT

Distribution of fixed and exchangeable ammonium were examined in three soil profiles of the Shrousts series from the Knobs region of eastern Kentucky. Shrousts soils (fine, mixed, mesic, Typic Hapludalfs) have high base status; exhibit strong, prismatic structure; and are derived from calcareous, high magnesium, soft (weakly cemented) clay shale. Soil pH ranges from 6.3 in the Ap horizon to 7.9 in the C. Analyses, using the Silva and Bremner procedure, showed considerable fixed NH₄⁺-N in all horizons of each profile. Mean fixed NH₄⁺-N in the profiles was 365 ppm for the Ap, 463 ppm for the B21, 483 ppm for the B22, 469 ppm for the C, and 454 ppm for the C horizons. Exchangeable NH₄⁺-N also increased with depth, values being about 1.2 to 1.5% of the fixed NH₄⁺-N values. X-ray diffraction analyses of the clays and silts revealed predominantly mica in the 2-0.2 and <0.2 μm fractions, with some vermiculite present, and large quantities of mica in the silt fractions. High correlation (r = 0.92) was found between fixed NH₄⁺-N and exchangeable NH₄⁺-N. A correlation exists between fixed NH₄⁺-N and mica + vermiculite content with an r value of 0.68. The fixed NH₄⁺-N in the lower horizons is presumed to be indigeneous, since no NH₄⁺-N has been added recently to the soil.

Additional Index Words: soil mineralogy, clay mineralogy, exchangeable ammonium.


The amount of indigenous fixed NH₄⁺ present in a soil depends to a large extent on the kind and amount of layer silicate minerals present. The soil minerals that are chiefly responsible for NH₄⁺ fixation are vermiculite, the mica, and montmorillonite (Allison et al., 1951; Bremner, 1959; Stevenson and Dhariwal, 1958). Dyal and Hendricks (1952) found that vermiculites have the greatest capacity to fix NH₄⁺, whereas illite may or may not fix NH₄⁺, depending on the degree of weathering and the K⁺ saturation on exchange sites. They also found that montmorillonite does not fix NH₄⁺ under moist conditions.

It has been known for some time that many soils have the ability to fix and hold substantial amounts of added NH₄⁺-N, and that some soils contain large quantities of indigenous fixed NH₄⁺-N. Bremner and Keeney (1966) note that most workers have defined fixed NH₄⁺ as that which is not extractable by 1M KCl at laboratory temperatures. Barshad (1951) proposed that fixed NH₄⁺ should be defined as NH₄⁺ that is not replaceable after long exposure to K⁺-salt solutions added to the soil.

The type of parent material from which a soil has formed also has a significant effect on the amount of fixed NH₄⁺ present in a soil profile. Adams and Stevenson (1964), in a detailed study of NH₄⁺ sorption and release from rocks and minerals, noted that NH₄⁺ was found along with nonexchangeable K⁺ in primary silicates. They concluded that the micas were primarily responsible for NH₄⁺ fixation by igneous rocks. Stevenson (1959) conducted a study of fixed NH₄⁺ in several specimens of shale and granite, using a modified Dhariwal and Stevenson (1958) method. He found that all specimens contained fixed NH₄⁺-N. The content of fixed NH₄⁺ in the shales varied between 330 and 420 μg N/g, whereas the content in granite rocks varied between 5 and 27 μg N/g. Stevenson concluded that rocks are able to accumulate N through retention of NH₄⁺ from rain water. He discovered that up to two-thirds of the total N in some Paleozoic shales occurs as fixed NH₄⁺ and speculated that native fixed NH₄⁺ may have been incorporated into the crystal structure at the time of synthesis of the minerals. Walsh and Murdock (1960) found that two shale-derived Wisconsin soils contained fairly large amounts of indigenous fixed NH₄⁺. The amounts of fixed NH₄⁺ found were related to the parent material from which the soil formed. Rich (1960) assumed that the fixed NH₄⁺ in muscovite parent material was substituted isomorphously for K⁺. He further concluded that, for any soil, there was a perpetual ratio between total K⁺ and fixed NH₄⁺ in the parent material.

A large number of workers have studied the distribution of fixed NH₄⁺-N through various soil profiles (Allison et al., 1953; Rodrigues, 1954; Hanway and Scott, 1956; Bremner, 1959; Stevenson and Dhariwal, 1958; Rich, 1960; Walsh and Murdock, 1960; Hinman, 1964). Meints and Peterson (1972) found that fixed NH₄⁺-N constituted 90-100% of the total inorganic N in certain Nebraska soils. Hinman (1964), working with some Canadian soils, found that the amount of fixed NH₄⁺ increased with increasing soil depth. Total amounts of fixed NH₄⁺ found through five horizons of a depth of 1.22 cm ranged from 2,500 lbs/acre in the loam surface horizons, to 1,461 lbs/acre in the more clayey subhorizons.

This study was initiated for the purpose of acquiring basic physical, chemical, and mineralogical characteristics of the Shrousts soil series. This paper examines the relationship between fixed NH₄⁺-N distribution and the mineralogy of the Shrousts series (Typic Hapludalf).

METHODS AND MATERIALS

These studies were conducted for three soil profiles of the Shrousts series. The profiles were sampled from Bath, Fleming, and Lewis Counties in the Knobs Region of eastern Kentucky. The Shrousts series is currently classified as a Typic Hapludalf. The soils are fine-textured, usually well-drained, and most commonly occur on narrow ridges and side slopes of the upland. Slopes range from 6 to 30%. The surface layer is a thin, dark grayish-brown silty clay loam. The subsoil is an olive-gray clay and is characterized by strong, prismatic structure. The parent material is a calcareous, high in exchangeable Mg, soft weakly cemented clay shale from the upper part of the Crab Orchard formation of Silurian geologic age. Descriptions and

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bulk horizon samples of each profile were taken from specially dug pits at each site. The bulk soil samples were air dried, ground to pass a 2-mm sieve, and thoroughly mixed before further analysis.

Particle size measurements were determined by the pipette method (SCS-USDA, 1967; Kilmer and Alexander, 1949). Additional samples were fractionated using 50 g of soil dispersed with 1N Na₂CO₃ following organic matter removal with H₂O₂. Sands (200–50 μm) were removed by wet sieving. Silt was separated into 50–20, 20–10, and 5–2 μm fractions by elutriation with water adjusted to pH 10 with Na₂CO₃ (Beavers and Jones, 1966). Clay fractions were separated into 2.0–2 μm and <0.2 μm fractions by supercentrifugation (Jackson, 1956).

Cation exchange capacity of each horizon was determined using the 1N NH₄OAc method of Pessagno et al. (1947). Exchangeable NH₄⁺ was determined with the procedure of Bremer and Kenney (1966). Fixed ammonium was determined with the method of Silva and Bremer (1966). Total N was determined using the procedure described by Bremer (1963).

Sufficient quantities of each of the clay and silt fractions separated by elutriation process were placed on ceramic tiles for X-ray diffraction measurements (Rich, 1975). The suction apparatus used to coat the tiles with clay was as proposed by Rich (1969). These fractions were either K-saturated by leaching 40 ml of 1N KCl through the clay or silt specimens followed by deionized water, or Mg-saturated by a similar manner using 40 ml of 1N MgCl₂ followed with 10 ml of deionized H₂O and 10 ml of 20% glycerol in water. The tiles were X-rayed using a Cu X-ray tube and Ni filter. The K-saturated tiles were X-rayed after heat treatment at 25, 110, 300, and 550°C. The Mg-saturated, glycerol treated tiles were X-rayed at 25 and 11°C.

The percentage of the various minerals was estimated using peak heights and d-spacings from the X-ray patterns. Values reported were rounded off to the nearest 5% although the accuracy for any given value may be ±10% of the stated value. For example, a value reported as 15% is considered to be in the range of 5 to 25%.

RESULTS AND DISCUSSION

The particle size distribution data (Table 1) show that the sand percentages were extremely low and silt percentages high in all horizons of the three profiles. Clay contents were consistently highest in the upper B horizons with greater than 50% clay present in all horizons of the profiles.

Soil pH (H₂O), Table 1, generally increased with increasing depth, becoming mildly to moderately alkaline in the Cr soil horizons. The high pH in the partially weathered Cr may be due to the high content of free bases, particularly Mg²⁺. The lower pH (5.0) in the B21t horizon of the Lewis County profile may have resulted from more intense weathering of this profile. This hypothesis is supported by the higher percentage of vermiculite found in this profile than in the other two profiles (Table 2).

The high CEC (Table 1) in the Ap horizons of the profiles can be ascribed dually to the high organic matter content and to the relatively high quantities of clay (>40%) in these horizons. The high clay content is primarily responsible for high CEC in the B horizons of the profiles. In all cases, the CEC generally decreased with increasing depth as organic matter content decreased.

Organic carbon content (Table 1) was high (3.4 to 4.4%) in the Ap horizons of the profiles and decreased with depth. The C/N ratio also decreased with soil depth with the organic C content decreasing more rapidly than total N.

Clay Mineralogy

Mica was the predominant clay mineral (Table 2) in both the 2-0.2 and <0.2 μm fractions of the Bath County profile. Kaolinite was found in both fractions of all horizons, with a lesser amount of vermiculite occurring primarily in the 2.0-μm fraction.

Mica contents found in the Fleming County profile were similar to the Bath profile, however, larger amounts of vermiculite were present. Mica in the <0.2 μm fraction tended to increase with depth.

The 2.0-μm and the <0.2 μm fractions of the Lewis County profile showed smaller amounts of mica than present in the other profiles and greater contents of vermiculite were present in the Ap, B21t, and Cr horizons. Vermiculite was present only in the Ap horizon of the <0.2 μm fraction and quantities of mica generally increased with increasing soil depth.

Silt Mineralogy

For the Bath County profile (Table 2), quartz predominated in the 50-20 μm and 20-10 μm fractions.

Table 1—Physical and Chemical properties of three Shrouds soil profiles.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Sand (2-0.05 mm) %</th>
<th>Silt (50-2 μm) %</th>
<th>Clay (&lt;2 μm) %</th>
<th>pH (1N H₂O)</th>
<th>CEC (meq/100 g) %</th>
<th>Organic C ppm</th>
<th>C/N</th>
<th>Total N ppm</th>
<th>Fixed NH₄⁺ ppm</th>
<th>Exch. NH₄⁺ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bath County</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ap 0–10</td>
<td>5.4</td>
<td>54.6</td>
<td>40.0</td>
<td>7.0</td>
<td>20.5</td>
<td>4.41</td>
<td>7.9</td>
<td>5,570</td>
<td>301</td>
<td>4.5</td>
<td></td>
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<tr>
<td>B21t 10-23</td>
<td>0.7</td>
<td>44.0</td>
<td>55.3</td>
<td>7.4</td>
<td>17.4</td>
<td>1.04</td>
<td>4.9</td>
<td>2,120</td>
<td>470</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>B22t 23-46</td>
<td>1.6</td>
<td>50.1</td>
<td>42.9</td>
<td>7.8</td>
<td>12.2</td>
<td>0.52</td>
<td>3.8</td>
<td>1,370</td>
<td>470</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>C 46-76</td>
<td>1.3</td>
<td>60.3</td>
<td>38.4</td>
<td>7.8</td>
<td>10.4</td>
<td>0.29</td>
<td>2.8</td>
<td>1,050</td>
<td>484</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>Cr 76-102</td>
<td>1.3</td>
<td>65.9</td>
<td>32.8</td>
<td>7.8</td>
<td>9.9</td>
<td>0.17</td>
<td>2.0</td>
<td>830</td>
<td>538</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td><strong>Fleming County</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ap 0–10</td>
<td>4.8</td>
<td>47.7</td>
<td>47.5</td>
<td>6.0</td>
<td>23.2</td>
<td>4.00</td>
<td>7.5</td>
<td>5,360</td>
<td>465</td>
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<tr>
<td>B21t 10-28</td>
<td>1.4</td>
<td>53.4</td>
<td>45.2</td>
<td>6.7</td>
<td>19.1</td>
<td>1.22</td>
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<td>2,010</td>
<td>509</td>
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<tr>
<td>B22t 28-46</td>
<td>2.9</td>
<td>49.0</td>
<td>48.1</td>
<td>7.9</td>
<td>14.3</td>
<td>0.52</td>
<td>3.9</td>
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<td>C 46-86</td>
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<td>49.4</td>
<td>8.0</td>
<td>9.3</td>
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<td>850</td>
<td>550</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Cr 69-102</td>
<td>1.3</td>
<td>59.7</td>
<td>39.0</td>
<td>8.0</td>
<td>9.3</td>
<td>0.17</td>
<td>2.0</td>
<td>850</td>
<td>550</td>
<td>7.2</td>
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</tr>
<tr>
<td><strong>Lewis County</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ap 0-15</td>
<td>6.2</td>
<td>52.0</td>
<td>41.8</td>
<td>6.0</td>
<td>25.5</td>
<td>3.43</td>
<td>7.2</td>
<td>4,790</td>
<td>340</td>
<td>4.8</td>
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<tr>
<td>B21t 15-25</td>
<td>0.8</td>
<td>36.2</td>
<td>63.0</td>
<td>5.0</td>
<td>28.5</td>
<td>0.58</td>
<td>4.5</td>
<td>1,300</td>
<td>412</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>B22t 25-51</td>
<td>0.8</td>
<td>35.9</td>
<td>63.3</td>
<td>6.7</td>
<td>29.4</td>
<td>0.52</td>
<td>3.7</td>
<td>1,240</td>
<td>424</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>B 51-76</td>
<td>1.5</td>
<td>48.6</td>
<td>49.9</td>
<td>7.5</td>
<td>20.8</td>
<td>0.29</td>
<td>2.7</td>
<td>1,070</td>
<td>408</td>
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<tr>
<td>C 76-97</td>
<td>2.2</td>
<td>58.3</td>
<td>39.5</td>
<td>7.9</td>
<td>15.2</td>
<td>0.17</td>
<td>1.9</td>
<td>920</td>
<td>430</td>
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<tr>
<td>Cr 97-127</td>
<td>1.3</td>
<td>60.0</td>
<td>38.7</td>
<td>7.6</td>
<td>15.3</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>541</td>
<td>6.9</td>
<td></td>
</tr>
</tbody>
</table>
The content of mica was high, however, even in the coarsest fraction. In all but the 50-20 μm fraction, the Cr horizon contained the greatest percentage of mica. Considerable amounts of mica were present, particularly in the 10-5 and 5-2 μm fractions of the Fleming County profile. The amounts of mica were fairly uniform in all fractions through all horizons. The mica contents of the Lewis County profile were somewhat lower, particularly in the finer fractions, than for the other profiles. A considerable amount of mica existed in all fractions however, with more being found in the C and Cr horizons than the A and B horizons.

Fixed and Exchangeable Ammonium in Relation to Mineralogy

Large amounts of fixed NH₄⁺-N (Table 1) were found in all horizons of the Bath County profile with 301 ppm NH₄⁺-N found in the Ap horizon and increasing to 538 ppm in the Cr horizon. This conforms to the trend found by Rodrigues (1954) and Hinman (1963). The fixed NH₄⁺-N increased with depth which coincided with the high percentage of clay and mica in the lower horizons and the influence of the shale parent material. Stevenson (1959) has shown that certain shales can contain 300-420 ppm indigenous fixed NH₄⁺-N. The silt fractions also (Table 2) contained large amounts of mica, which can contribute significantly to the amount of fixed NH₄⁺-N. The amount of fixed NH₄⁺-N in respect to total soil N showed a high of 64.8% in the Cr horizon of the Bath County site and a low of 5.4% in the Ap horizon at this site.

The Fleming County profile (Table 1), generally contained more fixed NH₄⁺-N than the Bath County profile. This is attributed to the higher clay contents, particularly in the Ap horizon. The clay fractions of this profile also contained more vermiculite than the Bath County profile, so more fixed NH₄⁺-N would be expected. The large amount of fixed NH₄⁺-N in the lower horizons of the profile can be ascribed to the presence of a larger percentage of mica and to the lack of weathering of the shale parent material. The exchangeable NH₄⁺-N increased as fixed NH₄⁺-N increased (Table 1), as in the Bath profile, being greatest in the Cr horizon.

The amount of fixed NH₄⁺-N in the Lewis County profile (Table 1) was similar to the other two profiles. In all profiles, the amount of exchangeable NH₄⁺-N (Table 1) increased with increasing amounts of fixed NH₄⁺-N, being the highest in the Cr and lowest in the Ap horizon. However, the ratio of exchangeable NH₄⁺-N to fixed NH₄⁺-N decreased with soil depth, which may be related to soil weathering.

The influence of mineralogy on fixed NH₄⁺-N is reflected in Fig. 1. A correlation exists between fixed NH₄⁺-N and mica + vermiculite content with an r
value of 0.68. The relatively unweathered Cr horizons contained the highest levels of fixed NH$_4^+$-N for all three sites and this nitrogen is considered to be indigenous (Table 1). These data suggest that a relationship exists in Shroust soils between the amount of minerals present that are considered to be capable of fixing NH$_4^+$ to the actual amount of fixed NH$_4^+$-N measured.

A good correlation exists between fixed and exchangeable NH$_4^+$-N with an $r$ value of 0.92. Some of the fixed NH$_4^+$-N is slowly released by weathering of the micas and expansion of the clay structure releasing NH$_4^+$-N to the exchangeable form. The difference in exchangeable NH$_4^+$-N content with depth suggests an equilibrium between the two forms of NH$_4^+$-N. The close correlation between fixed and exchangeable NH$_4^+$-N supports this hypothesis. Where there is more fixed NH$_4^+$-N, there would be expected to be more exchangeable NH$_4^+$-N released (e.g., in the lower horizons). The exchangeable NH$_4^+$-N as a percent of fixed NH$_4^+$-N tends toward slightly less availability with depth (Table 1), with the values all in the 1.2 to 1.5% range.

**LITERATURE CITED**