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Research article

INFLUENCE OF LONG TERM APPLICATION OF FERTILIZERS ON SOIL ORGANIC  
MATTER CONTENT<sup>1</sup>K.V. Naga Madhuri, <sup>2</sup>P. Chandrasekara Rao, <sup>3</sup>K. Vijay Krishna Kumar and <sup>4</sup>T. Prathima<sup>1</sup>Department of Soil Science, Regional Agricultural Research Station, Tirupati.<sup>2</sup>Dean of Agriculture, Acharya NG Ranga Agricultural University, Hyderabad.<sup>3</sup>Farmers' Call Center, Acharya NG Ranga Agricultural University, Hyderabad.<sup>4</sup>Department of Agro met, Regional Agricultural Research Station, Tirupati.

**ABSTRACT:** The soil samples were collected from the soils of Long Term Fertilizer Experiments that have been fertilized for the last 25 years from a) control plot (receiving no fertilizer/FYM); b) plot receiving 100% NPK fertilizer application and c) Plot receiving 100% N in the form of FYM, to study the changes in nature and amount of organic matter and these were compared with a similar adjacent soil under natural vegetation. The soil samples were collected from 0-15 cm (surface) and 15-30 cm (sub surface) layers. The humic substances were fractionated by Tyurins method. The total N and available N content was determined and C/N ratio was calculated. The humic acid was isolated, purified and analyzed for oxygen containing functional groups and spectral properties. It was observed that the soil under natural vegetation had a higher total N while the soil under continuous cultivation had higher available N. The C/N ratio of soil under natural vegetation was high compared to the soil under continuous cultivation. These values were high in surface layers compare to sub surface layers. The oxygen containing functional groups in Humic acid (HA) were high in soil under natural vegetation compared to the soil under continuous cultivation. The total acidity and COOH content of surface layers was high compared to sub surface layers in soils under both situations. Phenolic OH groups of subsurface layer was high in soil under natural vegetation and continuous cultivation indicating that this group in sub surface layers and high potential for interaction with clays and metal ions. The higher contents of total acidity and -COOH groups in soil under natural vegetation could be attributed to the difference in chemical composition and molecular weight of humic substances. The E4/E6 ratios of HA'S were less than 5.0 indicating high degree of condensation of aromatic humic acid. The potentiometric titrations of humic acids with standard 0.1 N NaOH indicated a gradual increase in pH with the addition of base thus indicating a high buffering capacity of humic acid. The potentiometric titration curves were sigmoid in nature indicating an apparent mono basic character and had a single break suggesting weak acidic character of humic acids. The conduct metric titrations of humic acids showed a slow increase in the initial stage followed by a steep increase at later stages. The apparent pKa values calculated from potentiometric titration data using Henderson-Hasselbalch equation varied from 5.24 to 5.68.

**Key words:** Organic matter, Humic acid, LTFE, Oxygen containing functional groups, C/N ratio

The organic matter content of soil is profoundly influenced by the cropping systems imposed on it. Numerous studies have shown the divergence in the nature of organic matter with tillage, fertilizer application and other agronomic practices (Janzen *et al*, 1992; Ladd and Russell, 1983). Shevotsva (1979) reported that the long term application of mineral fertilizers decreased the total carbon and nitrogen contents of soil over that of soil without fertilizers. Hence it is necessary to have a complete understanding of the nature of organic matter under natural vegetation and the changes brought about by cultivation practices under long term fertilizer application. We report here the effect of long term fertilizer application on changes in the soil organic matter content.

## MATERIALS AND METHODS

The soil samples were collected from the experimental plots under All India Coordinated Project on Long Term Fertilizer Experiments that have been fertilized for the last 25 days using rice crop. The soil samples were collected from: a) control plot not receiving either fertilizer or FYM; b) plot receiving 100% NPK in the form of fertilizer (120 kg N, 60 kg P<sub>2</sub>O<sub>5</sub> and 40 kg K<sub>2</sub>O/ha); c) plot receiving 100% N in the form of FYM. These were compared with a similar adjacent soil under natural vegetation. The soil samples were collected from two depths i.e., 0-15 cm (surface layer) and 15-30 cm (subsurface layer) and were analyzed for physicochemical and chemical properties by standard procedures (Jackson, 1967). The humic substances were fractionated and isolated by Tyurin's method (1931) as described by Kononova (1966). The humic acids were purified by dialysis (Wright and Schnitzer, 1959) and were analyzed for total acidity (Schnitzer and Gupta, 1965), -COOH groups (Schnitzer and Khan, 1972) and phenolic -OH groups. The spectral characteristics (E<sub>4</sub>/E<sub>6</sub> ratios and UV spectra) were recorded on spectronic 21-UVD-UV-VIS-Spectrophotometer. Potentiometric and conductometric titrations were also carried out.

## RESULTS AND DISCUSSION

The data on physicochemical characteristics, total and available N and C/N ratios are presented in Table 1. The organic matter content of soil was high under natural vegetation. The higher humus content could be directly related to the natural drainage condition. The better the drainage, lower is the organic matter content (Cole et al, 1989). The soil under natural vegetation did not have proper drainage. Ithori et al (1995) observed that combination effects were greatest in the surface horizon and losses in OM were directly related to the management practices, tillage and climate. When comparisons were made of total N content, the soil under natural vegetation had higher amounts of total N which the available N content was high in soil under continuous cultivation. The subsurface layer had lower amounts of total N. The higher amounts of available Nitrogen in the soil under continuous cultivation (100% NPK treated plot) could be attributed to the accumulation of nitrogen from the added fertilizers. The soil has been continuously supplied with nitrogen fertilizers and hence it could be possible to conclude that a major part of available N in soil came from inorganic source and not from organic source (Rasmussen et al, 1988; Janzen, 1987). Campbell and Zentner (1993) reported that addition of fertilizers on regular basis lead to an increase in N content of soil. The C/N ratio of soil under natural vegetation was high compared to soil under continuous cultivation. The ratio in subsurface layer was low because of high OC content. The C/N ratio showed narrowing tendency with depth indicating that humus in lower depth was rich in N content. Prasad and Singh (1982) observed that continuous use of FYM over 20 years helped in and improving the OM content of acidic soil. Among the treatments, incorporation of FYM resulted in an increase in OM content of soil. Janzen et al (1992) studied the OM and N content of the soil under long term crop rotation and fertilizer inputs. The fraction of OM was strongly correlated by them to the respiratory rates suggesting that OC fraction may be important C and energy sources for microorganisms. Further Rasmussen et al (1989) observed changes OM content and C/N ratios and related them to the amounts of organic manures added.

**Table 1: Physico Chemical Properties of Experimental Site**

| Treatments                             | Depth (cm) | pH   | EC (dS/m) | OC (g/kg) | Total N (1x10 <sup>-2</sup> ) % | Avail.N (1x10 <sup>-3</sup> ) % | C/N ratio | Texture |
|--|------------|------|-----------|-----------|---------------------------------|---------------------------------|-----------|---------|
| LTFE Control                           | 0-15       | 8.26 | 1.24      | 4.2       | 4.1                             | 9.8                             | 10.24     | Clayey  |
|  | 15-30      | 8.10 | 1.22      | 3.9       | 3.5                             | 8.2                             | 11.14     | Clayey  |
| LTFE 100% NPK                          | 0-15       | 8.00 | 1.80      | 3.7       | 7.5                             | 14.0                            | 4.93      | Clayey  |
|  | 15-30      | 8.08 | 1.83      | 3.1       | 6.3                             | 12.7                            | 4.82      | Clayey  |
| LTFE 100% FYM                          | 0-15       | 8.10 | 1.64      | 8.5       | 6.3                             | 12.0                            | 13.16     | Clayey  |
|  | 15-30      | 8.22 | 1.60      | 7.9       | 5.6                             | 11.3                            | 12.46     | Clayey  |
| Adjacent soil under Natural Vegetation | 0-15       | 8.15 | 1.90      | 10.6      | 8.1                             | 8.9                             | 14.16     | Clayey  |
|  | 15-30      | 8.22 | 1.92      | 9.1       | 7.3                             | 6.8                             | 13.08     | Clayey  |

The changes in quality of organic matter in soil as influenced by long term fertilizer application are presented in Table 2. For the reason beyond control, sufficient quantity of fulvic acid could not be extracted, isolated and purified. Hence the results are discussed with respect to Humic Acid (HA) fraction. Very small amounts of organic substances were lost due to decalcification by treatment with dilute HCl indicating that the HA content in soil was stable in nature. When the soil was treated with 0.1 N NaOH after decalcification, lot of HA was immediately released. This fraction (HA-1) combined with Ca and Mg and also immobile forms of  $R_2O_3$ , as it is extracted from soil after decalcification (Kononova, 1966). When the comparisons are made of HA-1 (expressed as % of air dry soil) under natural vegetation had higher amount of this fraction and the subsurface layer had lower content of this fraction. Among the treatments, the FYM treated soil had higher amount of this fraction. The humic acid fraction II(HA-II) released during treatment with 0.1 N  $H_2SO_4$  and successive extraction with 0.1 N NaOH represents the humic acid bound to stable hydrates of sesquioxides (Kononova, 1966). This fraction was high in soil under natural vegetation than the soil under continuous cultivation and the surface layer had higher amounts of this fraction than the surface layer. The substances extracted directly from the soil without decalcification by direct treatment with 0.1 N NaOH constitute HA bound to mobile forms of  $R_2O_3$ . This fraction was referred as HA-Ia (Kononova, 1966). The soil under natural vegetation had higher amount of HA-Ia as compared to soil under continuous cultivation. Considerably lesser of humus was present in the form of HA-Ib. this fraction, among the treatments was high in FYM treated plot while it was low in control plot. Since HA fraction I was obtained in sufficient quantities and formed the bulk of HA fraction in soil, the properties of this fraction was studied and is presented in Table-3. The phenolic -OH group content was high in soil under natural vegetation as compared to continuous cultivation. This could be due to differences in molecular weight and chemical composition of HA in these soils. The phenolic-OH group content was high in surface layer indicating high potential for their interaction with metal ions and clays.

**Table 2: Humic Acid Fractions of Experimental Site**

| Treatments                             | Depth (cm) | Humic acid fraction I |               | Humic acid fraction II |               | Humic acid fraction Ia |               | Humic acid fraction Ib |               |
|--|------------|-----------------------|---------------|------------------------|---------------|------------------------|---------------|------------------------|---------------|
|  |            | % of air dry soil     | % of total OC | % of air dry soil      | % of total OC | % of air dry soil      | % of total OC | % of air dry soil      | % of total OC |
| LTFE Control                           | 0-15       | 0.082                 | 32.12         | 3.10                   | 51.23         | 5.81                   | 23.34         | 39                     | 8.75          |
|  | 15-30      | 0.060                 | 30.18         | 3.02                   | 41.02         | 4.20                   | 20.18         | 1.80                   | 10.00         |
| LTFE 100% NPK                          | 0-15       | 0.085                 | 26.03         | 5.40                   | 51.10         | 6.03                   | 20.01         | 2.47                   | 6.03          |
|  | 15-30      | 0.070                 | 22.16         | 4.41                   | 50.98         | 5.91                   | 14.81         | 1.09                   | 7.35          |
| LTFE 100% FYM                          | 0-15       | 0.260                 | 48.12         | 9.02                   | 53.12         | 19.21                  | 33.81         | 6.79                   | 14.31         |
|  | 15-30      | 0.240                 | 39.06         | 8.23                   | 52.63         | 18.30                  | 27.18         | 5.70                   | 11.88         |
| Adjacent soil under Natural Vegetation | 0-15       | 0.460                 | 47.82         | 9.91                   | 55.21         | 10.01                  | 36.18         | 7.87                   | 11.64         |
|  | 15-30      | 0.350                 | 45.86         | 3.23                   | 54.30         | 9.12                   | 31.03         | 10.68                  | 14.83         |

**Table 3: Functional groups (Total acidity, -COOH and Phenolic OH group) content and E4/E6 ratios of humic acid extracted from experimental site**

| Treatments                             | Depth (cm) | Total acidity(me/g) | Carboxyl groups(me/g) | Phenolic-OH groups(me/g) | E4/E6 ratio |
|--|------------|---------------------|-----------------------|--------------------------|-------------|
| LTFE Control                           | 0-15       | 4.38                | 2.8(63.92)            | 1.58(36.08)              | 2.08        |
|  | 15-30      | 6.25                | 5.1(81.60)            | 1.15(18.40)              | 3.00        |
| LTFE 100% NPK                          | 0-15       | 3.75                | 1.8(48.00)            | 1.95(52.00)              | 1.97        |
|  | 15-30      | 5.76                | 3.9(67.71)            | 1.86(32.29)              | 3.02        |
| LTFE 100% FYM                          | 0-15       | 8.13                | 4.2(51.70)            | 3.93(48.30)              | 3.06        |
|  | 15-30      | 9.00                | 4.9(54.44)            | 4.10(45.55)              | 3.89        |
| Adjacent soil under Natural Vegetation | 0-15       | 9.38                | 4.6(49.04)            | 4.78(50.96)              | 5.01        |
|  | 15-30      | 10.63               | 5.9(56.09)            | 4.73(43.91)              | 5.93        |

(Figures in parenthesis indicate the contribution (%) towards total acidity)

The total acidity and -COOH groups were high in soil under natural vegetation than the soil under continuous cultivation and this could be attributed to differences in chemical composition and molecular weight of humic acid (Dkhar et al, 1986). The contents of total acidity and -COOH groups were high in subsurface layers than the corresponding surface layers. The ratio of optical densities at 465 and 665 nm has often been based for characterization of humic substances (Stevenson, 1982). This ratio (E4/E6) is independent of concentration of humic substances but vary with humic substances extracted from different soil types. This ratio was less than 5.0 (Table-3) and such a low value was reported by several workers (Nand Ram and Raman, 1981; Sachdev and Deb, 1982; Tomar et al, 1986). A low E4/E6 ratio indicated higher degrees of condensation of aromatic humic acid (Chen et al, 1977). The optical density of humic acids extracted from subsurface layer was higher than that obtained from surface layer, indicating that humic acid of subsurface layer possesses higher degree of aromaticity in the carbon atoms than those occurring in top layers. The UV spectra of humic acids were featureless with a decrease in optical density with an increase in wave length. The lack of absorbance in the UV region could be due to the fact that the UV spectra of lignin and coalified products are relatively uncharacteristic and that the humic substances were considered to be an intermediate state of development between lignin and coal (Schnitzer, 1978; Stevenson, 1982). The potentiometric and conductometric titration curves are plotted. The potentiometric titration curves were sigmoid in nature indicating an apparent monobasic character and had a single peak indicating weak acidic nature of HA. The apparent pKa values calculated from potentiometric titration data using Handerson-Hasselbach equation varied from 5.24 to 5.68 indicating weak acidic nature of humic acids. The conductometric titration curve of humic acid showed a drop in specific conductance at low values.

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