ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Physico – chemical characterisation of humic substances under long – term application of fertilizers and manures in rice – rice cropping sequence in an Inceptisol.

***M. Srilatha, P. Chandrasekhar Rao S. Harish Kumar Sharma and G.Padmaja**
Regional Agricultural Research Station, Acharya N.G.Ranga Agricultural University, Jagtial.

Manuscript Info

Manuscript History:

Received: 11 November 2013
Final Accepted: 28 November 2013
Published Online: December 2013

Key words:
Long term, humic acid, fulvic acid, functional groups, rice – rice cropping system).

Abstract

The present study was under taken during 2010 -11 in a long term fertilizer experiments on an Inceptisol to characterise the physico – chemical properties of humic fractions of soil organic matter at Regional Agricultural Research Station, Polasa, Jagtial, Acharya N.G.Ranga Agricultural University (A.P). Continuous addition of organic manures along with balanced inorganic fertilizers 100% NPK + FYM @ 10 t ha^{-1} enhanced the contents of humic fractions. HA content was high than FA. 100% NPK +FYM treatment recorded higher oxygen containing functional groups (Total acidity, carboxyl groups and phenolic – OH group) in FA than in HA. Total acidity in HA ranged from 7.7 to 9.4, carboxyl groups 4.6 to 5.8 and phenolic – OH groups ranged from 2.9 to 4.1 me g^{-1} whereas in FA it varied from 9.8 to 12.3, 5.9 to 7.8 and 3.6 to 5.1 me g^{-1} respectively.
Potentiometric titration curves obtained from both HA and FA are sigmoid in nature indicating their weak acidic nature. The E_4/ E_6 ratios of HA's were narrow ranging from 3.6 to 7.2 and FA's were wider (ranged from 6.4 to 8.4)

Introduction

Continuous use of inorganic fertilizers under intensive cropping systems leads to deteoration of soil properties resulting in decline in soil productivity. Under continuous cultivation soils are losing organic matter, faster than its replenishment. It has been established that the inorganic fertilizers alone can not improve the physical conditions of the soil. The results from study conducted by Kumar (2008) have also clearly shown the advantage of use of organic manures vis –a-vis inorganic fertilizers for over a long period. Poor recycling of organic sources leads to emergence of multiple nutrient deficiencies. Thus maintaining and improving soil fertility for sustainable agriculture is becoming more crucial due to increasing complexity of the nutritional problems.

Soil organic matter influences the plant growth through its effect on physical, chemical and biological properties of soil (Mamata *et al.*2007 and Stevenson, 1991). It has a physical function, in that it promotes good structure, thereby improving tilth, aeration, moisture movement and retention. It acts as an ion exchanger and store house for nitrogen, phosphorous, potassium and other nutrients. Fully decomposed soil organic matter is called as humus. Humus content is one of the most important factors determining the productivity of a soil because of multiple effects of humic substances such as release of plant nutrients, soil physical and biological conditions, checking the soil erosion, increasing the fertilizer use efficiency, environmental protection and reduced soil air and water pollution (Shirisha, 2002 and Flaig *et al.*1975).

Soil organic matter is not a homogeneous pool, but it consist organic components with a wide range of turn over times. It has many desirable characteristics which influence the soil physical, chemical and biological properties. The quantity and quality of organic matter representative of humic and non humic substances are greatly influenced by vegetation, climate, soil reaction and biological conditions. Humified organic matter will have a strong impact on soil fertility and may need to be taken in to consideration in development of fertilizer recommendations. Several workers reported that soil organic matter levels increased markedly in plots receiving FYM and long –term continued use of inorganic fertilizers containing N, P and K has increased soil organic matter levels.

The present investigation was taken up to study the impact of continuous use of fertilizers and manures and to characterise the humic fractions in soils under continuous intensive rice – rice cropping system.

Material and Methods

The present study is a part of the on going All India Coordinated Research Project on Long – term Fertilizer Experiments initiated in *kharif* 2000 in the experimental farm of Regional Agricultural Research Station, Polasa, Jagtial, Acharya N.G.Ranga Agricultural University (A.P) which lies at a Longitude of $78^{0}45'$ E to $79^{0}0'$E and $18^{0}45'$N to $18^{0}0'$N Latitude . The climate of the place is subtropical, the mean annual rainfall is 900 – 1500 mm. the soil, Typic Ustochrept, Black clay with clayey texture. The experiment was laid out in a randomised block design with 12 treatments, replicated four times, with a fixed and permanent plot size of 108 m^2(12 mX9m). The treatment details are as follows:

T_1 – 50%NPK , T_2 – 100%NPK, T_3 – 150%NPK, T_4 – 100%NPK +Hand Weeding, T_5 – 100%NPK+$ZnSO_4$ @ 10 kg ha^{-1}(in *kharif*), T_6 – 100%NP, T_7 – 100%N alone, T_8 – 100%NPK+FYM@ 5 t ha^{-1}(in each *kharif*), T_9 – 100%NPK-S, T_{10} – FYM @ 10 t ha^{-1}(in each *kharif* and *rabi*), T_{11} – Control (No fertilizers, No manures), T_{12} – Fallow (No crop , No fertilizers, No manures).

The optimal amounts of N, P_2O_5 and K_2O are 120-60-40 kg ha^{-1} respectively both in *kharif* and *rabi* seasons. Urea, SSP, MOP and $ZnSO_4$ are used as per treatments as source of N, P, K and Zn except in T_9 where DAP, urea and MOP are the nutrient sources. In 100%NPK +HW treatment, weeding is done by hand weeding as in other plots both chemical and hand weeding is taken up to control the weeds.

The soil samples were collected at the end of 10^{th} crop cycle and used for isolation of humic substances and were extracted, purified and characterised using standard procedures (Kononova, 1966). Humic acid and fulvic acids were estimated by separation after extracting with 0.5 N Na OH. Their differential solubility in alkali and acid was adopted as the criterion for separating them. Humic fractions were characterised for Functional groups like Total acidity (Schnitzer and Gupta, 1965), carboxyl groups (Schnitzer and Khan,1972) and Phenolic groups, Spectral properties (E_4/E_6 ratios), Potentiometric and Conductometric titrations.

Results and discussions

Results obtained from the humic fractions are presented in Table 1.The estimation of humic substances showed that the content of humic acid was high than fulvic acid in all the treatments. Humic acid content was ranged from 0.29 to 0.48% whereas fulvic acid content was 0.19 to 0.31%. Fulvic acid, although primarily considered to be humic acid precursors, may be humic acids degradation products as well. Similar results are reported by Santhy et al. 2001.

The content of humic acid increased with increased levels of fertilizer application and ranged from 24 to 51% over control (0.29%) and higher content of humic acid was recorded under 100%NPK+FYM (0.48%) followed by 150%NPK (0.44%) and in fallow treatment (0.42%).

Table 1. Effect of different treatments on soil humic substances (%) in post-harvest soil.

Treatments	Humic acid	Fulvic acid
50% NPK	0.36	0.23
NPK	0.39	0.25
150% NPK	0.44	0.30
NPK + HW	0.37	0.24
NPK + Zn	0.31	0.20
NP	0.32	0.22
N	0.36	0.23
NPK + FYM	0.48	0.31
NPK – S	0.35	0.23
FYM	0.42	0.27
Control	0.29	0.19
Fallow	0.42	0.27

The content of fulvic acid increased with increased levels of fertilizer application and ranged from 21 to 57% over control (0.19%) and higher content of humic acid was recorded under 100%NPK+FYM (0.31%) followed by 150%NPK (0.30%) and in fallow (0.27%) and FYM (0.27%) treatment.

100%NPK+FYM treatment recorded 65 and 63 % increase in HA and FA over control (0.29 and19% HA and FA respectively) , whereas only 100% NPK through inorganic fertilizer plot recorded less HA and FA content (34 and 31% of HA and FA respectively) than organic manure (FYM @ 10 t ha^{-1}) plot (44 and 42% of HA and FA respectively).

Highest content of humic (0.48%) and fulvic (0.31%) acid concentrations were recorded under 100%NPK+FYM which could be due to improvement of soil properties and favourable environment for the formation of humic substances in this treatment. Fulvic acid content was also recorded more in 150%NPK treated plot, addition of crop residues consequent to higher biomass yield might have produced more amount of fulvic acid. Lowest HA and FA concentrations were recorded in control (0.29% and 0.19% respectively).Similar results were reported by Gathala et al. 2007.

The organic carbon content increased with NPK doses so was the case with FA due to possible association between FA and total organic matter. The decomposition of added residues to contribute parts such as lignin derived phenolic units, carbohydrates or amino compounds yields the building blocks or substrates for humus formation The addition of organic manures over a decade resulted in the higher organic carbon content, improved crop growth when compared to unfertilized control plots. The plots which received 100%NPK+FYM recorded the highest organic carbon content. This might be due to consistent higher yields obtained in this treatment since inception. The relative increase in organic carbon due to FYM addition could be attributed largely to increased returns of organic materials and direct addition of organic matter through FYM along with recommended dose of NPK (Bharadwaj and Omanwar, 1994).

Characterisation of humic fractions:

The humic and fulvic acids isolated and extracted from different treatments were analysed for their functional groups. HA and FA's were highly relative natural polymers. Functional group analysis provides information about the occurrence of major functional groups in HA and FA and are thus an index of their activity.

The contents of oxygen containing functional group, obtained from HA and FA are presented in Table.2. Close perusal of data revealed that the oxygen containing functional groups viz., carboxyl, phenolic and total acidity were high in FA compared to HA. These results are in conformity with those Singh *et al*. (1986) and Sarmah and Borodoloi (1993).

Humic acids obtained from different treatments, total acidity ranged from 7.7 to 9.4 me g^{-1}, carboxyl groups 4.6 to5.8 me g^{-1} and phenolic - OH groups 2.9 to4.1 me g^{-1}, whereas in fulvic acid varied from 9.8 to 12.3 me g^{-1}, 5.9 to 7.8 me $g^{-1}$and 3.6 to 5.1 me g^{-1} respectively. Among the treatments higher total acidity was recorded in (FA 12.3 me g^{-1} and 9.4 me g^{-1}in HA) with application of 100%NPK+FYM.The data further suggested that FA's showed higher total acidity than HA's. Dkhar *et al*. (1987) observed that increase in total acidity with decreasing molecular weight was in consistence with increasing degree of oxidation of low molecular weight fractions.

Table. 2. Functional group (me g^{-1}) contents and E_4/E_6 ratios of humic and fulvic acids obtained from post harvest soils of rice.

Treatment	**Humic acid**				**Fulvic acid**			
	Total acidity	-COOH groups	Phenolic groups	E4/E6 ratio	Total acidity	-COOH groups	Phenolic groups	E4/E6 ratio
50% NPK	8.2	4.8	3.4	4.1	10.7	6.8	3.9	6.9
NPK	8.8	4.8	4.0	4.3	11.9	6.8	5.1	7.4
150% NPK	8.8	5.3	3.5	6.5	12.0	7.4	4.6	8.2
NPK + HW	8.3	4.8	3.5	4.5	11.7	7.0	4.7	7.6
NPK + Zn	8.4	4.8	3.6	4.4	11.2	6.3	4.9	8.0
NP	8.2	4.6	3.5	4.3	10.5	6.6	3.9	7.6
N	7.9	4.7	3.3	4.0	10.2	6.0	4.2	6.2
NPK + FYM	9.4	5.8	3.6	7.2	12.3	7.8	4.5	8.4
NPK – S	8.4	5.6	2.8	4.6	10.9	7.1	3.8	7.4
FYM	8.7	4.6	4.1	5.3	10.7	5.9	4.8	8.3
Control	7.7	4.8	2.9	3.6	9.8	6.2	3.6	6.4
Fallow	8.6	5.2	3.4	5.2	10.7	6.8	3.9	8.5

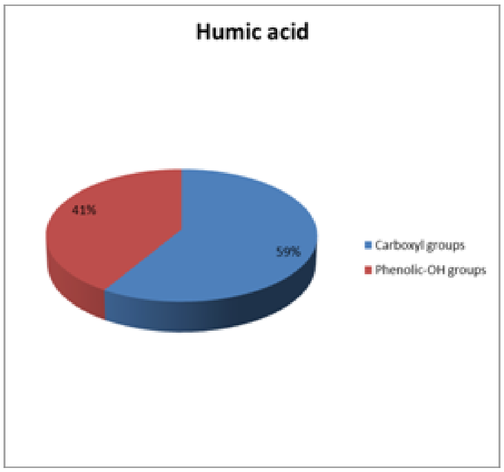
Similar trend was also observed in carboxyl group content. Among the treatments, higher carboxyl group content was recorded in (FA 7.8 me g^{-1} and 5.8 me g^{-1}in HA) in 100%NPK+FYM.The higher contents of carboxyl groups in FA may be due to their low particle weight because decarboxylation did not scan before polymerisation or condensation to high molecular weight. HA's, thus indicating degradation of HA's which may also result in high content of carboxyl groups (Lal and Mishra, 2000).

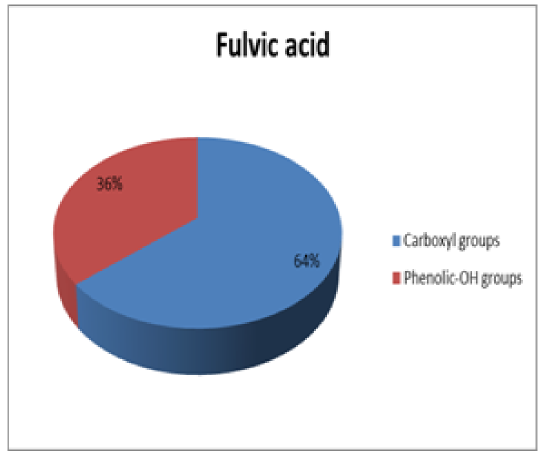
Among the treatments higher phenolic - OH group content was recorded in FA extracted from the treatment T_{12} (Fallow) 8.5 me g^{-1} and HA extracted from 100%NPK (5.8 me g^{-1}).

The contribution of phenolic – OH groups towards total acidity in FA ranged from 34.9 to 44.9% while it was 33.3 to 47.1% in HA. Similar results are reported by Lal and Mishra (2000).

The contribution of carboxyl groups towards total acidity in FA ranged from 55.1 to 65.1% whereas HA it varied from 53.0 to 62.3% indicating that %contribution of carboxyl groups towards total acidity of FA was higher than HA, but reverse trend was observed in case of phenolic – OH group (fig.1).

Fig.1. Per cent contribution of carboxyl and phenolic – OH groups towards total acidity in humic fractions





Characterisation of humic fractions for Spectral properties:

Measurement of absorption in different regions of electromagnetic spectrum has been used for qualitative and quantitative investigations on HA's and FA's (Stevenson, 1982). The ratio of optical densities at 465 and 665 nm is often used for characterisation of humic and fulvic acids. This ratio referred to as E_4/E_6 ratio, is independent of concentration of humic and fulvic acid but varies with humic material extracted from different soil types. (Lal and Mishra, (1999) ; Sailaja and Rao (2000) and Sujana Reddy *et al.* (2000).

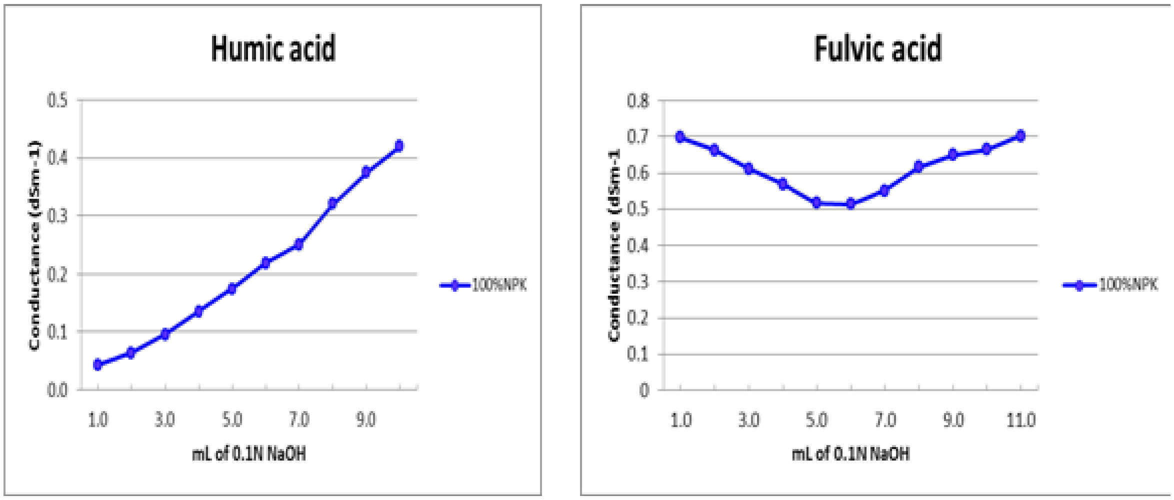
It was observed that E_4/E_6 ratios were related to the degree of condensation of aromatic humic acids. The optical densities of humic acids have lower values ranging from 3.6 to 7.2 and fulvic acids varied from 6.4 to 8.4 (Table .2). It could be due to the higher degree of aromaticity in carbon atom of HA. Lal and Mishra (2000) and Kaddali et al. (2001) also reported slightly higher E_4/E_6 ratios of FA than HA.

Potentiometric and conductometric titrations:

HA's and FA's extracted from different treatments showed gradual increase in pH with the addition of Na OH indicating high buffering capacity of these humic fractions (fig. 2 &3 respectively). The curves obtained for both HA and FA were sigmoidal in nature indicating their weak acidic characters. Similar results were reported by Nagamadhuri et al. (1998) and Sujana Reddy and Rao (2000).

HA and FA extracted from different treatments were conductometrically titrated against 0.1N Na OH. The results were presented in fig.4 &5 respectively. From the curves it could be observed that in the case of HA the conductance increased very slowly in the beginning and then followed a steep increase. The slow increase in conductance suggested that HA's behaved as weak acids. Similar results were reported by Sujana Reddy *et al*. (1999). In case of FA, the conductance decreased initially due to the neutralisation of strong functional groups, with further addition of Na OH, a constant or slight increase in conductance was observed suggesting the complexation of Na with FA and final increase in conductance is attributed to free Na^+. The higher conductance of FA compared to HA may be due to purification of these fractions, and the HA dialysed were almost free of ions, a lower conductance was observed (Adhikari *et al*. 1972).

Fig. 2. Conductometric curves of humic and Fulvic acid.



Conclusions

Humic and fulvic acids extracted from different treatments showed that among humic fractions, humic acid content was more than fulvic acid. Analysis for oxygen containing groups (total acidity, carboxyl groups and phenolic – OH groups content) were high in fulvic acid than humic acids. Spectral characteristics like E_4/E_6 ratios were also studied and found narrow ratios in HA than FA's.

References

Adhikari,M., Chakravarthy, G and Hazra, G.C.1972. Fulvic acid metal complexes, *Journal of the Indian Society of Soil Science.* 20 (4): 311-321

Kononova, M.M.1966.Soil Organic Matter. Pergamon. Press.pp.400-410.
Kumar,A. 2008. Direct and residual effect of nutrient management in maize (*Zea mays*)– wheat (*Triticum aestivum)* cropping system. *Indian Journal of Agronomy*. 53 (1): 37 -41.

Lal, J.K and Mishra, B. 1999. Visible Absorption spectroscopic investigation of soil humic substances. *Journal of Research BAU.* 11 (2): 135 – 140.

Lal, J.K and Mishra, B. 2000. Physico chemical characterization of humic substances isolated from some soil series. *Journal of Research BAU.* 12 (2): 179-185.

Nagamadhuri,K.V., Rao,P.C and Raju, A.S. 1998. Influence of natural vegetation and continuous cultivation of organic matter content in soils of Rajendranagar, Hyderabad, India. Paper presented at 16th World Congress of Soil Science held at Agropolis, Montpellier Cedex, France during August 22 – 26, 1998.

Santhy, P., Muthvel, P and Selvi, D. 2001. Status and Impact of Organic Matter Fractions on yield, uptake and available nutrients in a long term fertilizer experiment. J*ournal of the Indian Society of Soil Science*. 49(2): 281-285.

Sarmah, A.C and Bordoloi, P.K. 1993. Characterization of humic and fulvic acids extracted from two major soil groups of Assam. *Journal of the Indian Society of Soil Science.* 41(4): 642-648.

Sujana Reddy, M and Rao,P.C.2000. Characterisation of humic metal ion interactions in Alfisol and Vertisols by potentiometric methods. *Journal of the Indian Society of Soil Science.* 48 (3): 596 -598.

Sujana Reddy, M and Rao,P.C.2000. Stability constants of Cu(II), Fe (II), Mn (II) and Zn (II) with humic acids extracted from an Alfisol and a Vertisol in relation to their plant availability. Paper presented at 65th Annual Convention of Indian Society of Soil Science at National Bureau of Soil Survey and Land Use Planning Nagpur, during December, 27 -30, 2000.

Schnitzer, M. and Khan, S.U.1972. Humic Substances in the environment. Marcel – Dekker, New York.

Sujana Reddy, Rao, P.C and Raju, A.S. 1999. Interaction of humic acid fractions obtained from Alfisol and Vertisol of Acharya N.G. Ranga Agricultural University, Rajendranagar campus by absorption spectroscopic methods. Journal of Environmental Bio chemistry.

Foot Note

1. Scientist, sriluss02@gmail.com, Department of Soil Science and Agricultural Chemistry, Regional Agricultural Research Station, Jagtial, District: Karimnagar- 505 529 (Andhra Pradesh)

2. Professor & University Head, Department of Soil Science and Agricultural Chemistry, ANGRAU, Hyderabad.

3. Associate Professor, Department of Soil Science, College of Agriculture, Hyderabad.

4. Associate Professor, Department of Soil Science, College of Agriculture, Hyderabad.