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***Review article***

# EFFECT OF LONGTERM APPLICATION OF FERTILIZERS ON SOIL ORGANIC MATTER – A CRITICAL REVIEW

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Soil organic matter is one of the most important natural resources and since time immemorial man has recognized that soil fertility may be maintained or improved by adding organic manures. The importance of soil organic matter in influencing the physical characteristics, controlling microbial activity, supplying plant nutrients and a number of other processes is well documented. Hence the effect and nature of organic matter has been studied by several workers in different disciplines. For this review, it is proposed to cover only such aspects of studies on soil organic matter which are relevant. The relevant literature is presented here under the following heads.

## Composition of Soil humus

The soil organic matter is one of the most complex materials existing in nature and contains naturally occurring organic compounds of plant and animal origin. Humus represents the heterogeneous complex of numerous compounds of plant, animal and microbial origin and their decomposition products. This has been divided into two groups, non-humic substances and humic substances (Kononova,1966). Non-humic substances include various nitrogenous and non-nitrogenous compounds like proteins and their degradation products, carbohydrates, fats, waxes, resins, pigments and numerous low molecular weight compounds. On the other hand, humic substances are not related to any of the existing known groups of organic chemistry and form a large part of total reserves of humus (80-90%). These are yellow or brown to black coloured, acidic, poly disperse substances of relatively high molecular weight (Stevenson, 1983). Based on solubility, the humic substances are broadly divided into three classes. (a) Humic acid (alkali soluble and acid insoluble). (b) Fulvic acid (acid and alkali soluble) and (c) Humin (insoluble in both acid and alkali).

Chaudhury and Saha (1973) studied the distribution and nature of organic matter along the profiles of some rice soils of West Bengal and reported remarkable variation in the organic matter content and total nitrogen per cent of top (0-15 cm) layers which contained higher organic matter and total 'N' than lower (15-30 cm) layers.

Banerjee and Chakraborthy (1977) from their studies on nature, distribution and composition of organic matter in surface soils of West Bengal found that there is a regular difference in nature, distribution and composition of organic matter. A moderate moisture regime, slightly acidic to neutral reaction and fairly intensive microbiological activity are the main factors for formation of humic acid while high moisture regime, alkaline reaction and less microbiological activity in formation of fulvic acid.

Tomar et al (1986) characterized the organic matter in soils of widely different climatic zones and observed that humus content was highest in pine forest Utifluvent of Morni Hills and lowest in Tripura under maize-jute rotation.

**Nature of organic matter in soils under natural vegetation and forests:**

Five profiles of North-Western Himalayas representing soils developed under natural vegetation in different altitudinal belts of North-Western Himalayas was studied by Dhir (1973). Results indicated that humus in high altitude soil profile was overwhelmingly fulvic with fractions associated with free sesquioxides predominating. Further the humic acid molecule has a low degree of condensation and thus in close to fulvic acid. The humus in middle altitude soil profile was less fulvic and it showed an increase in fractions associated with divalent cations. This trend is not maintained in lower middle altitude profile where as in low altitude profile humus becomes exceptionally humic with fractions associated with divalent cations dominating.

From the studies on nature and composition of humus in major soil orders of Rajasthan, Joshi (1981) observed that Alifisols and Mollisols were characterized by preponderance of humic acid where as in Entisols and Vertisols had less of humic acid and significantly higher amounts of non-humic and fulvic acid fractions was observed. The nature of fulvic acid and humic acid in soils were not varied very much different in these soils.

The amount of humus varied from 0.023 to 0.88 per cent constituting 7.9 to 37.0 per cent of the total organic carbon and it was invariably higher in 'A' horizons of the soils under forest and grass covers. The humic and fulvic acid fractions constituting 56.4 and 43.5 per cent of the total humus were dominant in forest grasslands and cultivated soils respectively (Gupta et al., 1982).

From their observations on forms, distribution of humic acid and fulvic acid component in soils under deciduous and coniferous forests. Mukhopadhyay et al. (1982) observed that, in the soils under conifers, fulvic acid fraction constitutes more than 68 per cent of the humus where as other deciduous forests the values were much less. On passing from foot-hills to higher elevations, the humic acid/fulvic acid ratio altered towards preponderance of fulvic acids. The exchange capacity of humic acids extracted from deciduous forest belt was some what higher than that of coniferous forest soils. Humic acids in the former soils were more aromatic in nature while there was a predominance of aliphatic groupings in case of coniferous forest soils.

The humic and fulvic acids obtained from surface samples (0-15 cm.) showed higher total acidity than the corresponding fractions from sub-surface horizons (15-30 cm.) isolated from forest soils of Tarai region of Uttar Pradesh (Challa et al., 1985). UV spectral studies showed featureless absorption spectra with neither maxima nor minima.

Humic acids and fulvic acids extracted from forests and cultivated soils were characterized by Dkhar et al. (1986) for elemental analysis, functional group determination, $E_4/E_6$ ratio and UV and IR spectroscopy. Fulvic acid fraction predominated in forest soils compared to that of cultivated soils. The organic carbon and nitrogen contents of humic acids from surface soils were higher than from sub-surface soils. The oxygen contents of fulvic acids from surface layer were higher than those from subsurface layer. The contents of functional groups were higher in forest surface soils than in cultivated soils.

Singh et al. (1986) analysed humic and fulvic acid frctions of hill soils of Mizoram in terms of their functional groups and reactiveness with sesquioxide content and observed that soils did not indicate any appreciable movement of the organic matter induced deposition of sesquioxide as that in a Spodosol.

Sharma and Gupta (1987) observed that the amount of humus varied from 0.145 to 1.59 per cent in forest soils of Himachal Pradesh and constituted 33.2 to 83.2 per cent of total organic carbon.

**Nature of organic matter in cultivated soils:**

Unger (1968) studied the changes in organic matter and nitrogen during the 24 years of wheat tillage and cropping practices and concluded that the tillage practice resulted in significant difference in soil organic matter content when a wheat-fallow cropping system was used. Soil total nitrogen content was significantly affected by tillage practices used for wheat-fallow cropping system.

While studying changes in soil fertility under long term cultivation of fodder crops and grasses, Singh et al. (1977) observed a decline in organic carbon content from medium to low class inspite of application of 'N' fertilizers at recommended doses.

Rasmussen et al. (1980) observed changes in nitrogen and carbon in a wheat-fallow system as influenced by crop residue treatment and showed the evidence of substantial loss of organic matter during 50 years of wheat cultivation. The changes in nitrogen and carbon were primarily confined to top 20 cm layer of soil.

The amount of organic matter in native Prairie and in an adjacent cultivated field were compared with the output from a simulation model describing organic matter dynamics by Voroney et al. (1981). Seventy years of cultivation decreased the organic carbon content by 36 per cent in soil profile at the mid slope position. Management practices such as straw removal and cropping sequence had short term effects on the rate of depletion of soil organic carbon. Similar equilibrium levels of soil organic matter were predicted hundred years of cultivation in simulation studies.

Tiessen and Steward (1983) evaluated the effects of cultivation on organic matter composition in size fractions and observed that organic matter loss during 65 years of cultivation on a coarse-sandy loam soil showed a similar distribution and magnitude across size fractions while heavy clay soil was characterized by greater stability of silt and clay associated organic matter which lost only 10 per cent during seventy years of cultivation.

Paired range land and cultivated soils were characterized along toposequences by Aguilar et al. (1988) in South-Western North Dakota to evaluate the changes in organic carbon and total phosphorus resulting from forty four years of cultivation. Cultivated and virgin grassland soils were compared on adjacent landscape segments in order to quantify losses or gains of organic carbon, nitrogen and total phosphorus. Losses were generally greatest from the upper landscape where erosion resulted in significant reductions in solum thickness.

Burke et al. (1989) predicted regional pattern of carbon in range and cultivated soils and observed that organic carbon increased with precipitation and clay content and decreased with temperature. Analysis of cultivated and rangeland soils for organic matter content indicated that organic carbon losses due to cultivation increased with precipitation and that relative organic carbon losses were lowest in clay soils.

Effect of cropping system on quantity and nature of organic matter was studied by Dayegamne (1989) and his results showed that rotation over a ten year period had no effect on soil organic matter, but increased the carbon content of humic acid and enhanced the biological activity in soil in comparison with monoculture.

Wagner (1989) studied the long term effect of wheat, red clover and timothy on soil organic matter and concluded that after hundred years of continuous cultivation, fifty per cent of soil organic matter originated from native prairie species. When the prairie was first cultivated a rapid loss of organic matter was attributed to labile pool. Improved crop and soil management had positive effects on the soil organic matter content.

A study conducted by Havlin et al. (1990) to determine the effects of tillage, crop rotation and fertilizer nitrogen on soil organic carbon and nitrogen revealed that fertilizer nitrogen improved soil organic carbon and nitrogen only slightly. Crop management systems that included rotations with high residue producing crops and maintenance of surface residue cover with reduced tillage resulted in greater soil organic carbon and nitrogen which improved soil productivity.

The Characteristics of humic acids from two arable soils in Taiwan were studied by Chen and Wang (1992) using spectroscopic methods. Their results showed that the differences in organic carbon content of arable surface soils were mainly due to the differences in vegetation. Tillage practice affected humic acids with heavier molecular weight from the alluvial soil than those with lighter molecular weights from the red soil. The NMR results have shown that the aromticity of surface soil humic acids increased with increased tillage.

The effects of cultivation and the regrowth of bush fallow on soil organic matter and phosphorus fertility were evaluated by Tiessen et al. (1992) using six adjacent plots with different histories of cultivation. Organic carbon and nitrogen content increased with increasing fallow period, the plots with twelve years of cropping + fertilizer and liming. Whereas the plots with one year of fallow after six years of cropping showed the lowest organic carbon levels.

The loss of soil organic matter when a forest was converted to agriculture was investigated by Woomer (1992). Clearing of miombo and establishment of maize-based agriculture on a sandy Alfisol resulted in a decline in total organic carbon content. The removal of natural forests, shifting cultivation and commercial cultivation of maize resulted in annual carbon losses of 0.15 and 0.14 t/ha.

Effect of shifting cultivation, organic matter and nutrient status of an upland volcanic soil in North-West Cameroon were evaluated by Aweto and Bongfen (1993). Soil characteristics under the cropping phase of shifting cultivation were compared with those in an adjoining ten years old grass savanna fallow protected from burning. The organic matter contents of the 0-15 cm., and 15-30 cm., layer of cultivated soils were lower than the levels in the grass savanna control plots.

The morphological characteristics and organic matter contents of seven soils cultivated for twenty years were compared with those of four uncultivated soils by Higuchi and Kashiwagi (1993). Their results revealed a decrease of the A-horizon thickness due to cultivation and the contents of organic matter in most cultivated soils were markedly lower than those of the uncultivated soil.

Ihori et. al. (1995) conducted an experiment to study the effect of cultivation on soil organic matter and reported that total nitrogen and carbon were highest in native land and lowest in cultivated land. The loss due to cultivation was 26 per cent of total carbon and 29 per cent for total nitrogen.

**Nature of organic matter under long-term fertilizer and manure application**

Shevtsova (1979) reported that the long-term application of low to medium doses of mineral NPK fertilizers for 20-50 years did not have a negative effect on organic matter of derno-podzolic soils. Mineral fertilizer applied over a long period decreased the total carbon and nitrogen content over that of a soil without fertilizer. Prolonged application of manures had pronounced effect on humus content of soil, particularly in ploughed layer.

Continuous use of FYM and NPK fertilizers over a period of twenty years helped in maintaining and improving physical properties and increase in total organic carbon content of an acid red loam soil while the application of fertilizer nitrogen alone lightly deteriorated soil physical properties. A significant change in organic carbon and nitrogen resulted with the use of fertilizers, manure and lime (Prasad and Singh, 1980; Rasmussen et al., 1980).

The results of the study by Sachdev and Deb (1982) on effect of application of organo-mineral fertilizers on humic acid characteristics in alluvial soil indicated that the formation of humic acid was affected by the type of fertilizer treatment to some extent and the differences occurred mainly in the functional group content. No significant variations were observed in the absorbance characteristics in the visible and IR spectra of the humic acids by any of these treatments.

Odell et al. (1993) observed changes in nitrogen and organic carbon in the dark coloured soil on the murrow plots during seventy years under different cropping systems and treatments. Their results indicated that crop rotation plus appropriate fertilizer application produced the highest crop yields and also maintained soil nitrogen and organic carbon at the highest levels.

Chen and Wang (1987) showed that the application of green manures at 22.5 – 30 t/ha for live years increased the soil organic matter by 7.3 to 33.6 per cent compared with control. In addition, green manuring improved the quality of soil organic matter, increased the active organic matter content and total humus content.

Data for a brown soil under a rotation of Maize – Soybean (Zhang et al., 1987) for a period of five years indicated that nitrogen reduced the organic matter content and all the fertilizers affected humus content while pig manure application increased the organic matter content.

Soil organic carbon and nitrogen were measured forty four years after establishment of a long term experiment to evaluate tillage and fertilizer effects in a winter wheat fallow rotation by Rasmussen and Rohde (1988) on coarse-silty mixed typic Haloxevoll. Nitrogen fertilization increased soil nitrogen linearly in all tillage treatments with 18 per cent of the applied nitrogen incorporated into the soil organic fractions.

Muthuvel et al. (1989) reported that in a four year cotton-pearl millet rotation in dry land Vertisol annual application of FYM to provide 40 kg. $ha^{-1}$ nitrogen markedly increased the soil organic carbon content.

From the results of a long term field experiment conducted by Kostyukevich and Alekseychik (1990), it was shown that application of moderate amounts of mineral fertilizers decreased the humus content with an annual loss of 1.4 per cent of the initial amount in an acid soil.

Angers and Dayegamne (1991) reported that relative to the un-manured soil, biannual application of 40 and 80 t $ha^{-1}$ manure increased carbon and nitrogen after 10 years of application of solid cattle manure.

Few studies conducted by Campbell and Zentner (1993) in Western Canada have assessed the influence of crop rotations and fertilization on soil organic matter content on medium textured acidic haptoborsol that has been cropped for 24 years and monitored soil organic matter in 0-15 and 15-30 cm depth. Further they reported that the amount of organic matter in the top 0-15 cm depth of soil varied depending on the amount and nitrogen content of the crop residue returned to the land.

**Functional groups present in organic matter fractions:**

Wright and Schnitzer (1978) studied the oxygen containing functional groups of organic matter of a podzol soil and reported that material from $B_h$ organic matter was high in total acidity and –OH groups than Ao material. There was little difference in carboxyl content. Schnitzer and Desjardins (1966) reported that humification was associated with carboxyl, alcoholic groups and a lesser extent of carbonyl groups.

A study on characterization of humic acid and fulvic acid extracted from different Indian soils conducted by Nanda Ram and Raman (1981) and their results indicated that humic acids contained more carbon and less oxygen than did the fulvic acid. Fulvic acids contained more carbon and less oxygen than did the fulvic acid.

Fulvic acids shows higher O/H values but lower C/H values than humic acids. Fulvic acids were more acids as compared to humic acids. From the study of molecular formulate it was evident that the cultivated soils showed a much lower carbon and hydrogen content than the corresponding forested soils.

The functional group composition of humic acid and fulvic acid isolated from forest and cultivated soils were given by Dkhar et al. (1986). Their data showed that total acidity, carboxyl and phenolic –OH contents of fulvic acids were more than those of humic acids. The higher content of total acidity and carboxyl groups in the forest surface soils over that of cultivated surface soils was observed. The contents of total acidity and carboxyl were high in humic acid or fulvic acids extracted from cultivated sub-surface samples than those of forest sub-surface soils. Similary, the humic acid and fulvic acid of well drained forest and cultivated soils possessed higher content of total acidity and functional groups in comparision to their poorly drained counterparts. The $E_4/E_6$ values of humic acid and fulvic acids of cultivated soils were relatively lower than that of forest soils.

Two methods of total acidity determinations of humic substances were compared by Piccolo and Camci (1990), the $Ba(OH)_2$ method and a direct potentiometric titration after elusion of humic substances through a cation exchange resin results showed that $Ba(OH)_2$ method was more accurate method.

## Spectral properties of organic Matter fractions:

Eight profiles representing major soil order4s in different agro-climatic regions of Rajasthan were studied by Joshi (1981) for humus composition. He characterized nature of humic acid and fulvic acid by optical density ratios (E4/E6) and coagulation threshold values. Narrow $E_{4\text{-}}/E_6$ ratios and lower threshold values of humic acids of Entisols, Mollisols and Vertisols of Banswara profie were observed whereas wider $E_4/E_6$ ratio and higher threshold values of humic acid was observed for Kota soils. Fulvic acids of all the profiles studied had wider $E_4/E_6$ and higher threshold values compared to humic acids.

The partition coefficients and $E_4/E_6$ colour ratios of fulvic acids and humic acid fraction were studied by Prasad and Sinha (1982). Their results indicated a highly significant relationship between the values of $K_a$ and $E_4/E_6$ ratio. The $E_4/E_6$ ration showed inverse relationship with molecular weight of fulvic acid fraction.

Challa et al. (1985) in their study on humic substances from forest soils of Tarai region reported UV spectra which showed a featureless absorption spectra with neither maxima nor minima but with maximum absorption values at 200 – 350 nm wave lengths.

According to Dkhar et al. (1986), the IR spectra of fulvic acid differed from those of humic acid mainly in 1700 $cm^{-1}$ in the region of 1200 $cm^{-1}$ IR spectra and $E_4/E_6$ ratio indicate that humic acid and fulvic acids are more aromatic in nature in cultivated soils than those of forest soils.

**Polymaleic acid as a model for Soil Fulvic Acid:**

Despite a long history of interest and research, the soil humic substances till defies a precise chemical description, because of their inherent complexity and heterogeneity, in contrast to clays which are crystalline and can be had in pure forms. Anderson and Russell (1976) proposed that polymaleic acid (PMA) could serve as a model for fulvic acid, after observing remarkable similarities between the two materials in elemental analysis. IR spectra and a number of hydrolysis products. Polymaleic acid was prepared by the polymerisation of maleic anhydride in the presence of pyridine and washed free of excess pyridine with chloroform and acetone. The similarities to soil fulvic acid which were found to be especially striking were: (a) the occurrence of vicinal carboxyl groups readily converting to anhydrides. (b) unsaturation which accounts for IR absorption bands near 1620 $cm^{-1}$. On the basis of their analytical data, they concluded that fulvic acid consisted mainly PMA type structures. Linehan (1977) stated that PMA while structurally similar to soil fulvic acid, had the added advantage of structural homogeneity, and suggested that it could be possible to obtain structural modifications during the polymerization for PMA for better understanding of the relationship between nature and growth promoting properties.

Spiteller and Schnitzer (1983) reported that there were lot of similarities between PMA and Soil fulvic acid in a number of Characteristics, but minor differences could be observed in fluorescence, $^{13}C$ = NMR spectra and in oxidation products and in oxidation products. Compared to fulvic acid, PMA appeared to be better orgasnized and more homogeneous at the molecular level, richer in olefin structures and less aromatic structures.

From their studies with polymaleic acid, Raman and Rao (1996) concluded that there were similarities between polymaleic acid and soil fulvic acid and polymaleic acid could be used as a synthetic model for soil fulvic acid. Further, they used it for studying the characteristics of clay – PMA polymer complexes as synthetic models for naturally occurring clay – humus complexes for studying the nature of interactions between soil fulvic acid and homoionic clays.

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