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# Transformation of a Coal Fertilizer Ammonium Polycarboxylate and Potentialities of Coal Produced Nitrification Inhibitors

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**Abstract** : *A laboratory experiment was conducted on a Typic Ustochrept soil to study the transformation of a coal fertilizer ammonium polycarboxylate (AMP) and efficacy of coal acids (CA) and nitrohumic acid (NHA) as nitrification retardars. During 35 days (d) of incubation period, at field capacity AMP showed lower soil* $NH_4^+$*-N and* $NO_3^-$ *– N than urea. Difference in* $NH_4^+$*-N and* $NO_3^-$*-N contents between urea and AMP gradually narrowed down with time. From 28d onwards AMP showed slightly higher* ($NH_4^+$)*-N than urea. Both CA and NHA inhibited effectively* $NH_4^+$*-N oxidation up to 28d. Under flooding, all the treatments showed maximum soil* $NH_4^+$*-N on 7d except AMP. Up to 14d* $NH_4^+$*-N content was in the following sequence : urea + CA > urea + NHA ≈ urea > AMP > control. From 21d, AMP was superior to rest of the sources. The CA was more effective than NHA under flooding. Average soil* $NO_3^-$*-N content was < 4 ppm on application of urea and < 1 ppm in AMP. Effects of CA and NHA were not reflected in* $NO_3^-$*-N content of the soil samples.* (**Key words:** Urea transformation, ammonium polycarboxylate, coal acids, nitrohumic acid, nitrification inhibitors)

Urea is the major nitrogen fertilizer used in India. But owing to its rapid hydrolysis, a major part of applied N is lost from the soil-plant system. To reduce these losses various approaches like, use of slow release fertilizers and nitrification inhibitors (NIs) have been extensively tried but their high cost restricts their wide use. Therefore, there is a need for developing inexpensive and more efficient N fertilizer materials and NIs that function over a broad range of soil conditions. In India, large quantities of coal are being mined every year (207 Mt in 1988-89) against the reserves estimated at 155,902 Mt (Statesman's Yearbook, 1990-91, p. 642). Bulk of good quality coal is being diverted to metallurgical operations, whereas a substantial amount of low grade coal remains to be properly utilized. If such coal is oxidized with nitric acid beyond the humic or nitrohumic acid (NHA) stage, the latter is converted into much simpler products called polycarboxylic acids, predominantly aromatic in character. Such products are composed of mixture of organic acids like benzene polycarboxylic acids and/or polycarboxylic acids of naphthalene, anthracene, phenanthrene or similar aromatic moieties which constitute the macromolecular matrix of coal structure (Singh *et al.* 1979). The gross mixture of polycarboxylic acid or the coal acids (CA), on suitable ammoniation produces a new kind of coal fertilizer called ammonium polycarboxylate (AMP). It has about 14-16 per cent

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**Present address* : Soil Chemistry Unit, Resource Management Program, International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, Andhra Pradesh, 502 324 total N of which 9-10 per cent in readily available form, mostly in ammonium and partly in amide forms (Mazumdar *et al.* 1981). Some work on these materials have been carried out (Singh *et al.* 1979, Mazumdar *et al.* 1981), but, detailed information regarding the behaviour of AMP in soil at different soil-water contents is lacking. Similarly the usefulness of CA and NHA as nitrification inhibitors has not been studied in detail. The present investigation was undertaken to evaluate AMP as a source of N and to evaluate CA and NHA as nitrification inhibitors.

## Materials and Methods

**Table 1.** *Some properties of nitrohumic acid (NHA), coal acids (CA) and the coal fertilizer ammonium polycarboxylate (AMP).*

| Property | NHA | CA | AMP |
|---|---|---|---|
| Appearance | Granular powder | Granular powder | Porous granular solid |
| Colour | Brownish black | Chocolate brown | Chocolate brown |
| Solubility | Insoluble in water | Soluble in water and most of the polar organic solvants | Soluble in water |
| Hygroscopicity | - | Somewhat hygroscopic,particularly in rainy season | Hygroscopic particularly in rainy season |
| C (%) | 62 | 51 | 46 |
| H (%) | 4 | 2 | 4 |
| Total N (%) | 5 | 6 | 15 |
| Available N (%) | - | - | 9 |
| Nitro-N + (other forms) | - | 6 | 6 |
| O-COOH (%) | 9 | 23 | - |
| CEC [cmol ($p^+$) $kg^{-1}$] | 300-350 | 700-800 | - |

An investigation was carried out on 0-15 cm surface samples from Mehrauli sandy loam (Typic Ustochrept) soil of the Institute farm, New Delhi. The soil was air-dried and ground to pass a 2 mm sieve. Some of the properties of the soil were as follows : pH (1 : 2.5) 8.3, EC 0.4 dS $m^{-1}$, CEC 8.6 cmol ($p^+$) $kg^{-1}$, organic C 0.5%, sand 71.3%, silt 13.3%, and clay 15.4%. Ammonium polycarboxylate (AMP), CA and NHA were supplied by the Central Fuel Research Institute (CFRI), Dhanbad. Some properties of these materials are presented in table 1.

Soil samples (500 g) were weighed into large mouthed white plastic bottles and to it the following treatments were given : Control, urea-N (100 ppm), urea-N (100 ppm) + CA, urea-N (100 ppm) + NHA and AMP-N (100 ppm). The CA and NHA were applied @ 10 per cent of the urea-N. One set of soil samples was incubated at field capacity and another set under flooded condition at 30° C. The loss of water by evaporation was replenished at regular intervals. Each treatment was triplicated and all the bottles were randomly (CRD) arranged. Mouth of the bottles were covered with perforated lids. Samples were taken weekly up to 35d and analysed for $NH_4^+$-N and $NO_3^-$-N + $NO_2^-$-N by extraction with *2M* KCl and distillation of the filtrates with MgO and Devardas alloy (Keeney & Nelson 1982).

## Results and Discussion

The data on the $NH_4^+$-N content of the soil samples at field capacity show that urea maintains higher amount of $NH_4^+$-N than AMP between 7 and 21d (Table 2). This indicates that urea mineralizes faster than AMP during the initial period of its application. After 21d, both the sources were at par with respect to $NH_4^+$-N. These results also indicate that AMP behaves as a slow release material during the first 21d probably because of presence of nonfunctional N (heterocyclic) (Sanyal *et al.* 1979) which lowers mineralizing capacity. These results further show that the two compounds differ in the nature of N present. The most likely form of N in AMP seems to be amide of organic acids since this is produced by neutralization of aromatic polycarboxylic acids with ammonia (Mazumdar *et al.* 1981). Incorporation of CA and NHA in conjunction with urea resulted in more accumulation of $NH_4^+$-N up to 28d. Irrespective of sources, $NO_3^-$-N content in soil increased significantly with incubation period (Table 2). This

**Table 2.** *Effect of N source and incubation period on $NH_4^+$-N and $NO_3^-$-N contents in the soil*

| | Field capacity | | | | | Flooding | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Incubation period (days) | | | | | Incubation period (days) | | | | |
| N source | 7 | 14 | 21 | 28 | 35 | 7 | 14 | 21 | 28 | 35 |
| | $NH_4^+$ – N (ppm) | | | | | | | | | |
| Control | 7 | 15 | 21 | 14 | 12 | 30 | 28 | 29 | 27 | 25 |
| Urea | 16 | 44 | 34 | 23 | 17 | 67 | 63 | 52 | 49 | 47 |
| Urea + CA | 20 | 50 | 42 | 28 | 18 | 75 | 72 | 50 | 49 | 46 |
| Urea + NHA | 17 | 49 | 40 | 28 | 19 | 68 | 65 | 53 | 48 | 43 |
| AMP | 13 | 26 | 30 | 24 | 21 | 49 | 54 | 56 | 55 | 59 |
| CD (P=0.05) | N source = 0.78 | | | | | N source = 1.7 | | | | |
| | Days = 0.78 | | | | | Days = 1.7 | | | | |
| | N source × days = 1.73 | | | | | N source × days = 3.78 | | | | |
| | $NO_3^-$ + $NO_2^-$ – N(ppm) | | | | | | | | | |
| Control | 18 | 30 | 32 | 38 | 40 | 0 | 0 | 0 | 0 | 0 |
| Urea | 55 | 65 | 66 | 72 | 73 | 4 | 4 | 2 | 2 | 2 |
| Urea + CA | 46 | 53 | 65 | 70 | 74 | 4 | 3 | 3 | 2 | 2 |
| Urea + NHA | 52 | 56 | 63 | 71 | 74 | 4 | 2 | 2 | 2 | 1 |
| AMP | 26 | 47 | 53 | 66 | 65 | 1 | 1 | 1 | 2 | 1 |
| CD (P=0.05) | N source = 1.18 | | | | | N source = 0.63 | | | | |
| | Days = 1.18 | | | | | Days = 0.63 | | | | |
| | N source × days = 2.64 | | | | | N source × days = 1.38 | | | | |

was because of nitrification process which was more prominent after 7d. Data in table 2 also show that urea is better than AMP in the maintenance of $NO_3^-$ - N in soil. The difference is significantly high in the early period and narrows down in the later stages. It indicates clearly that AMP behaves as a slow release N carrier. Application of CA and NHA with urea showed lower $NO_3^-$-N in soil as compared to urea. This is due to inhibition effect of CA and NHA on the process of nitrification. The lower values of $NO_3^-$ -N on 7 and 14d are indicative of the fact that inhibition effect was mainly during first two weeks and there were not much differences in $NO_3^-$ -N contents between urea alone and urea with CA and NHA after 14d. At field capacity, total inorganic N ($NH_4^+$-N + $NO_3^-$-N + $NO_2^-$-N) also showed much higher values on application of urea than AMP up to 28d. From 28d onwards, there was almost similar release of $NH_4^+$-N + $NO_3^-$-N from all the sources except the control. Since AMP has been found to maintain lower amounts of $NH_4^+$-N + $NO_3^-$–N in the soil, it may prove to be inefficient source of N to those arable crops which need more N during early stage of their growth. Use of CA or NHA with urea found effective to show lower total mineral N in soil up to 14d and higher afterwards.

At flooding, maximum $NH_4^+$-N was observed on 7d and thereafter gradually decreased with time in all the sources except AMP (Table 2). Application of AMP showed gradual increase in $NH_4^+$-N content in soil throughout the incubation period. Examination of the data (Table 2) shows that CA is a better retarder of nitrification than NHA under flooded condition also. However, as was noted under field capacity, retardation effect was for two weeks only. At flooded condition $NO_3^-$-N was found very low in all the treatments (Table 2). Maximum 4 ppm $NO_3^-$-N was observed up to 14d on application of urea alone or with NIs and thereafter it was reduced to < 2 ppm in rest of the sampling days. Lower $NO_3^-$-N concentration at flooded condition is expected, because at restricted oxygen diffusion, nitrification occurs only in the flood water and in the thin (< 3 mm) oxydized surface soil layer (Savant & De Datta 1982). Low $NO_3^-$-N content in submerged soils also may be due to rapid disappearance of $NO_3^-$-N presumably through nitrification - denitrification processes (Reddy & Patrick 1986; Aulakh 1989).

From the present investigation it can be concluded that AMP acts as a slow release N fertilizer and more suitable under flooded condition. Both CA and NHA have the promise as nitrification inhibitors at field capacity, whereas under flooded condition only CA seems to be effective.

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