# ON THE AGROBIOLOGICAL ACTIVITY OF OXIDATIVELY AMMONIATED COAL*

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Since the late 1950's, much of the research effort devoted to the development of coal-based plant nutrients has shifted from humates to so-called 'nitrified' or 'nitrogen-enriched' coal (NEC). Aside from studies of the mechanism (1) and kinetics (2,3) of the oxidative ammoniation reaction by which this material is prepared, recent literature thus contains several reports of more or less extended growth trials with NEC in India (4), Canada (5) and Australia (6). And active interest in the outcome of these investigations, or in initiation of similar projects, has been expressed in the United States, the Soviet Union, New Zealand, and a number of Central European countries.

In large measure, this shift reflects growing awareness that ammonium humates or nitro-humates are unlikely to command much attention outside relatively small specialty or 'luxury' markets (5). But despite reports - including some from our own laboratories - that plant reaction to NEC frequently equals or betters gains accruing from the use of ammonium sulphate or nitrate, the nutrient value of NEC remains questionable. Indian findings (4) that NEC, typically less effective than nitrogenous mineral fertilizers during the opening years of an extended test program, subsequently equals or surpasses ammonium sulphate are not substantiated by Canadian (5) and Australian (6) experience. And observations that secondary treatment of NEC with $HNO_3$ and aqueous $NH_4OH$ yields products that <u>do</u> release substantial quantities of N have been found to be connected with the fact that such treatment also converts some associated mineral matter into assimilable nitrates (5).

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Since publication of their field trial results for the period 1958-64, Indian investigators (7) have come to concur in the view that NEC does not contain much 'available' N; and there is a concensus that their observations may have been directly influenced by increased moisture retentivity and improved structure of the impoverished soils in which the growth trials were conducted. (That coal or oxidized coals rich in humic acids can effect such improvements has been known for some time (8)). However, because gains resulting from application of $HNO_3$-oxidized NEC or mixtures of NEC with nitrogenous mineral fertilizers seemed on occasion rather greater than could prima facie be accounted for by the inorganic nitrogen (or urea-N) in this way introduced into a soil, belief in NEC's nutrient value has been revived by two alternative suggestions (5,6,9). One raises the possibility that NEC releases N at rates which, although too small to be measured by conventional laboratory tests, are yet great enough to affect plant life over the more extended period of a full growth cycle. And the second invokes possible synergistic behaviour of a mixture containing NEC and a conventional nitrogen source. The present study was undertaken with a view to testing the validity of these notions.

## Experimental

(i) Materials: Nitrogen-enriched coal was prepared by treating a subbituminous coal (70.5% C, 5.1% H, d.a.f.) with gaseous ammonia and air at 300°C. The reaction was carried out in a small electrically-heated fluid-bed reactor (3) and furnished three stock samples with, respectively, ∿9%,∿11% and ∿17% N.

Proceeding from these samples, a range of nutrient formulations which allowed simultaneous evaluation of all major compounding variables were prepared. Table 1 shows the form of this 'grid' as used in the growth trials. A similar 'grid', only differing in minutiae from that shown in Table 1, was employed for nitrogen-release rate measurements. In both sets, unreacted coal, $HNO_3$-oxidized coal, and mixtures of these with urea or ammonium nitrate were used as controls.

Total (analytical) nitrogen contents of test nutrients and control materials were determined by the standard Kjeldahl method and/or by a standardized gas chromatographic technique (which employed a Hewlett-Packard FM 185 C-H-N Analyzer). Nitrogen contents of plant matter harvested from the pots (cf. below) were measured by the Kjeldahl method.

Table 1. Materials 'Grid' used for Greenhouse Growth Tests with Grass

| | | | |
|---|---|---|---|
| Coal | 65/115 | + 5% $NH_4NO_3$ | impregnated |
| | | | dry mixed |
| | | + 5% urea | impregnated |
| | | +10% urea | dry mixed |
| | <115 | + 5% $NH_4NO_3$ | impregnated |
| | | +10% urea | dry mixed |
| Coal, HNO -oxidized | 65/115 | +10% urea | impregnated |
| NEC-I (~17% N) | 65/115 | + 5% urea | impregnated |
| | | | dry mixed |
| | <115 | + 5% $NH_4NO_3$ | dry mixed |
| | | + 5% urea | impregnated |
| | | + 1% urea | dry mixed |
| NEC-II (~9% N) | 65/115 | + 5% urea | impregnated |
| | | | dry mixed |
| | <115 | + 5% $NH_4NO_3$ | dry mixed |
| | | + 5% urea | impregnated |
| | | + 1% urea | impregnated |
| NEC-II, $HNO_3$-oxid. | 28/48 | + 5% urea | impregnated |
| | <115 | + 1% urea | dry mixed |
| | | + 5% urea | impregnated |

(ii) Nitrogen-release rates were studied by incubation of nutrient-amended soil and subsequent determination of $NO_3$- by the standard phenol disulphonic acid method (10). The soil was a 1:1 v/v mixture of washed sand and black Chernozemic loam that had been thoroughly leached with distilled water, air-dried, and screened to <12 mesh. Test nutrients were hand-mixed into this substrate to provide 100 ppm (analytical) nitrogen, and the mixtures then placed in styrofoam cups over a vermiculite base (cf. Figure 1). Incubation, in total darkness to prevent algal growth, was carried out in a controlled-environment chamber at 25°C and 95-98% r.h. for 19 days, and results cited below represent arithmetic averages of four replicates.

(iii) Growth Trials: Plant responses to the various test nutrients under greenhouse conditions were measured by growth of Reed Canary Seed in <12 mesh 1:1 v/v Chernozemic loam/washed sand, to which nutrients equivalent to 100 ppm (analytical) N had been added with the aid of a small hand-churn. Each plastic 5 in. greenhouse pot held 1000 gms. of soil and was seeded with ∿1.0 gm grass seeds. Moisture conditions were in all instances maintained near field capacity, but in order to facilitate germination, moistened filter paper discs covered the seeds during the first few days of the trials.

After germination, the paper discs were removed, and growth allowed to continue to a height of 5-6 in. before being cut. The harvested material from each pot was then immediately placed into tared paper bags, oven-dried at 60°C, and weighed. Tests were terminated after the third cut, when it was evident that all supplies of 'available' nitrogen had been exhausted.

## Results and Discussion

Although the quantities of nutrient added to the soil mixture were in each case predicated on the supposition that all nitrogen forms were equally 'available' - and hence adjusted to provide 100 ppm analytical N - it is convenient to test the actual 'availability' of this added nitrogen by assuming that all N chemically fixed in coal and coal products is agrobiologically inert. Experimental results have therefore been graphed as functions of 'effective N', i.e. of nitrogen contained in the admixed urea or ammonium nitrate.

With respect to the results of N-release rate measurements, this procedure yielded a plot of the form shown in Figure 2, where release rates are expressed as percentages of the urea-rate. Table 2 identifies the various symbols which discriminate between the major nutrient types. Because of the relatively high nitrogen content of NEC itself, formulations of NEC and urea (or ammonium nitrate) cluster in the region of low 'effective N' (mostly at <25 ppm N); but like the other nutrient materials, and in common with them, they all lie close to a straight line which proceeds from the urea-point (100/100) to intersect the ordinate within the range of values recorded with unamended soil. For the entire set, N-release is thus, within the error limits of the experimental method, directly proportional to the 'effective' nitrogen application.

An analogous result is obtained from the growth trial data, which were likewise treated as if all nitrogen in coal, $HNO_3$-oxidized coal and NEC were entirely inert.

Yields of (dried) plant matter obtained in each of the three harvests are shown in Figure 3 (whose symbols are identified in Table 2). The inset reproduces the 2nd harvest results for <30 ppm 'effective N' (which are virtually coincident with the corresponding 3rd harvest yields and have therefore been isolated for greater clarity of presentation). And the limits within which replicates of any one set varied are defined by the vertical lines through the data points.

Table 2. Representation of Test Nutrients

| | Fig.2* | Figs.3-5 |
|---|---|---|
| Untreated coal | —○— | —○— |
| $HNO_3$-oxidized coal | —◑— | —□— |
| NEC-I (∿17% N) | —⬒— | —△— |
| NEC-II (∿ 9% N) | —□— | —▽— |
| NEC-III (∿11% N) | —◨— | |
| NEC-II, $HNO_3$-oxidized | —△— | —*— |
| Fuller's Earth | —●— | |

* Except for the few preparations marked *, which contained ammonium nitrate, all nutrients carried 'effective N' in urea.

Nitrogen recoveries - i.e. the variation of each harvest's 'per pot nitrogen' with 'effective N' rates - are presented in Figure 4; and the (percent) nitrogen contents of the dried plant matter are shown in Figure 5. In both diagrams, the symbols are the same as those used in Figure 3 (cf. Table 2).

Inspection of the 1st harvest yields (cf. Fig. 3) shows that short-term growth which does not seriously deplete the available nitrogen supplies is an unreliable index of nutrient performance: when 'effective' N applications exceed 5-10 ppm, yields tend to be almost entirely insensitive to variations in available nitrogen*. But taken in conjunction with subsequent harvest data, they point to a marked lack of utility of NEC.

Due, it appears, to minor amounts of hydrolyzable nitrogen which exists in NEC in reaction intermediates (1), most NEC samples caused slight initial improvements over the soil control (cf. 1st cut data, Fig. 3)**. However, these nitrogen sources are evidently rather quickly exhausted. And by the time of the 2nd harvest, growth supported by NEC or mixtures of NEC with small amounts of urea or $NH_4NO_3$ - which have by then also been substantially exhausted - is indistinguishable from growth in unamended soil or soil containing coal.

Nor does a further lapse of time - to the 3rd harvest, when all 'effective' N-supplies have been totally depleted - improve matters. Growth remains stunted at the soil control level.

There is perhaps, as comparison of the 1st and 2nd harvest data in Figs. 3, 4 and 5 suggests, another way of looking at plant growth. There appears to be a disposition for production of plant matter to take precedence over the demands of 'normal' plant chemistry; and so long as it is not actually acute, a soil-nitrogen deficiency will tend to be reflected in lowered plant-nitrogen rather than in reduced formation of plant matter. After a high 'effective' N application, 2nd harvest yields (and, consequently, 'per pot' nitrogen recoveries) will thus be greater than after a small application - but if the nitrogen supply is by that time beginning to be seriously depleted, the nitrogen content of the plant matter will be lower. Where plant composition rather than quantity is important - e.g., if

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* By implication, fertilizer testing above this (or some equivalent) minimum N-level is therefore liable to lead to quite erroneous inferences. It seems probable that failure to recognize this point has contributed to the conflicting reports on NEC performance.

** An analogous initial gain is observed with $HNO_3$-oxidized coal in which, as already noted, varying amounts of 'available' N exists in mineral matter-based assimilable nitrates.

the protein content of the plant is, for various reasons, an overriding criterion - obervations of growth per se may therefore be misleading. But as Figs. 4 and 5 clearly show, NEC makes as little contribution to composition as to growth: as soon as initial supplies of (hydrolyzable or admixed) 'effective' nitrogen are exhausted, plant responses to NEC-reinforced soil are in no way different from response to unamended soil.

Both facets of the growth trials thus lead to the conclusion that NEC - regardless of whether it is used alone or in combination with another nitrogen source - is an essentially inert and agrobiologically useless, material. No evidence was found to sustain the view that NEC functions as a slow N-release nutrient or that mixtures of NEC and urea or $NH_4NO_3$ behave synergistically.

This conclusion is in no way modified by the length of the ammoniation reaction period (which governs the nitrogen level of NEC) or by the manner in which urea or ammonium nitrate are introduced into NEC-based formulations. Neither the N-release test nor the growth trials were able to differentiate between NEC with, respectively, ∿9% and ∿17% N; to distinguish between formulations containing urea or $NH_4NO_3$ in particulate or impregnated forms; or to define effects of NEC particle size.

Significantly, NEC also failed to influence utilization of 'effective' N. Nitrogen balances established from the initial 'effective' N-application and the total N-recovery by plant matter over the entire growth period show an efficiency of ∿50% regardless of the type or form of test nutrient*.

There remains, of course, a possibility that the period of this study's growth tests was too short to detect a slow progressive chemical change leading to N-release from NEC. But a line of reasoning proceeding from this argument is difficult to sustain unless it is supposed that chemical change is induced by specific soil microorganisms. We would, in this connection, observe

(i) that even minimal amounts of nitrogen released from NEC would, had they in fact been released, have been

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* Because of the relatively small amounts of 'effective' nitrogen supplied to the soil, and because of the inevitable errors attending determination of analytical nitrogen, the actual range was fairly wide. But there were no indications whatever of systematic dependence of efficiency on nutrient type.

detected at the time of the 3rd harvest;

(ii) that possible slow abiotic oxidation of NEC in a well-aerated soil (and consequent formation of a nitrogen-rich humic acid capable of releasing a portion of its nitrogen content) is unlikely in view of the failure of $HNO_3$- oxidation to produce such a change; and

(iii) that the chemical inertness of NEC (1) also rules out abiotic reduction to a nitrogen-releasing material.

## Acknowledgments

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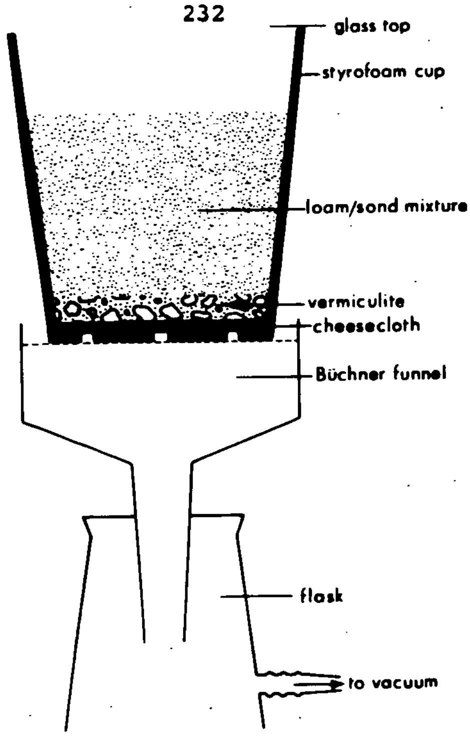



Figure 1. Container for Nitrogen Release Rate Measurements (as set up for preliminary leaching of soil mixture).

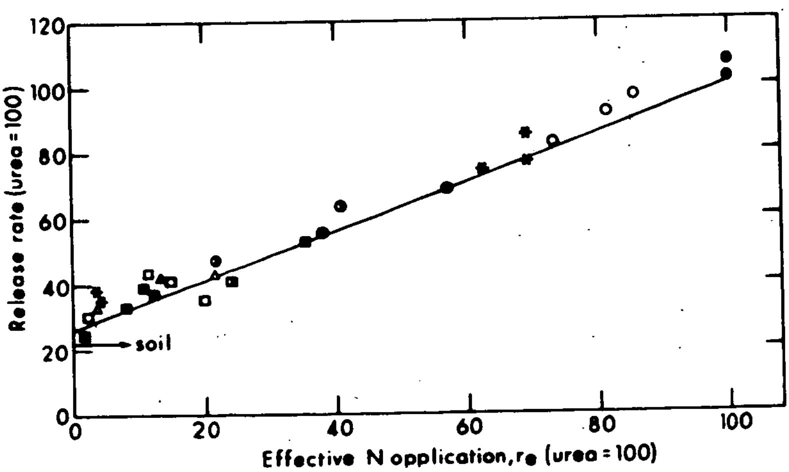



Figure 2. Nitrogen Release as Function of "Effective" Nitrogen Application. (For meaning of symbols, cf. Table 2).

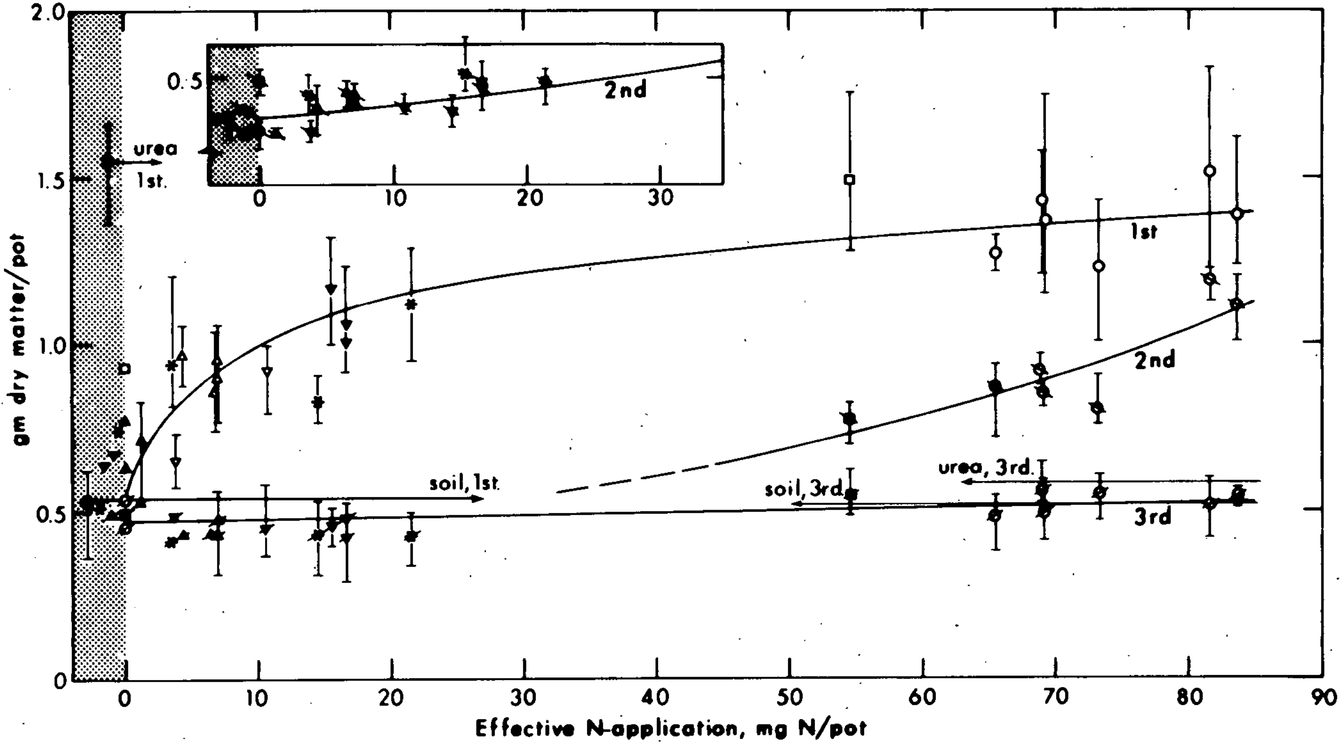



Figure 3. Growth Rate as Function of "Effective" Nitrogen Application (cf. Text and Table 2 for meaning of symbols).

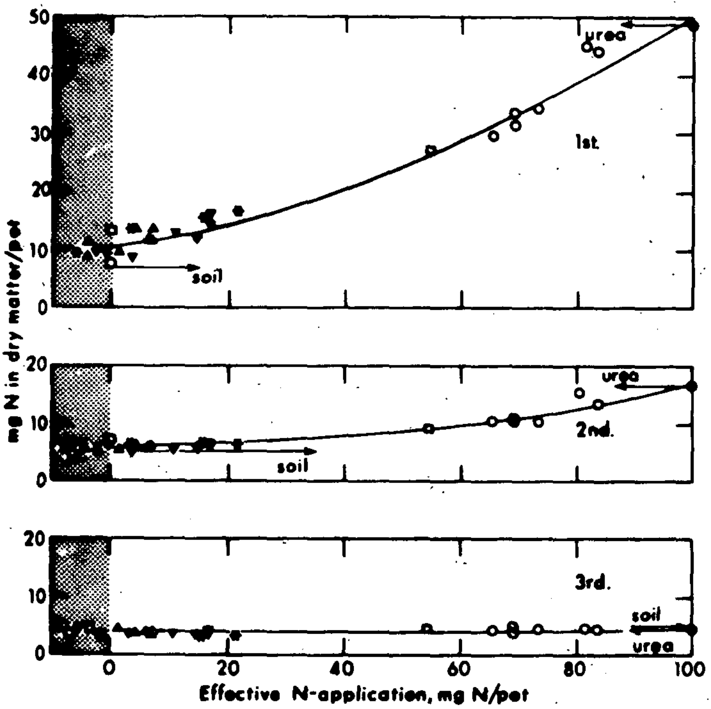
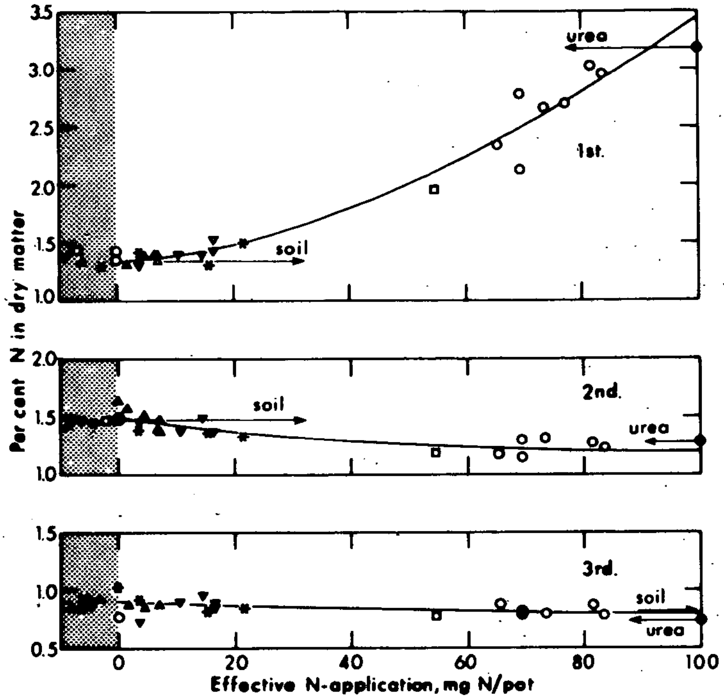



Figure 4. Nitrogen Recovery as Function of "Effective" Nitrogen Application. (cf. Text and Table 2 for meaning of symbols).




<u>Figure 5.</u> Nitrogen Contents of (Dry) Plant Matter as Function of "Effective" Nitrogen Application. (cf. Text and Table 2 for meaning of symbols).