STUDIES ON THE USE OF UREA AS A FERTILIZER FOR TEA IN CEYLON I—INTRODUCTION AND PRELIMINARY OBSERVATIONS

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This paper which is the first of a series to be published on urea fertilization, is intended to serve as an introduction to the subject. It deals with the history of the use of urea as a fertilizer, its chemistry and biochemistry and its behaviour in the soil and plant. Preliminary observations made on experiments carried out on tea soils and tea, in Ceylon, are also reported.

Interest in the use of urea as the chief nitrogen fertilizer for tea was given an impetus by the decision of the Government recently to set up a plant to manufacture urea in Ceylon. Indirectly, urea has been employed as a fertilizer for a considerable length of time, since it is the main source of nitrogen in excrements of mammals. Urea which is the chief end product of nitrogen metabolism in mammals is excreted mainly in the urine. An average human (adult) excretes about 30g urea (Finar 1953), and mature cattle an equivalent of 210 g urea per day (Peterson *et al.* 1956). Because of this origin of urea from living sources it is classified as an organic compound. However, urea ($NH_2.CO.NH_2$) was the first organic compound to be synthesized from an inorganic substance (ammonium cyanate NH_4NCO). This historically important synthesis was achieved in 1928 by Wöhler, who stated that he "can prepare urea without requiring a kidney of an animal, either man or dog" and exploded the belief of the necessity of a "vital force" for production of organic compounds.

$$NH_4NCO \longrightarrow NH_2.CO.NH_2$$

The use of urea as a synthetic nitrogen fertilizer began only with the cheap industrial preparation in 1920s from calcium cynamide (CaN.CN).

$$CaN.CN + 3H_20 \longrightarrow H_2N.CO.NH_2 + Ca(OH)_2$$

Nowadays urea is prepared from liquid ammonia and carbon dioxide;

$$2NH_3 + CO_2 \longrightarrow NH_4CONH_2 \longrightarrow NH_2.CO.NH_2 + H_20$$

this reaction which requires high temperatures and pressures produces ammonium carbamate (NH_4CONH_2) as an intermediate which is dehydrated to give urea. The urea solution obtained is then used for producing solid urea. Two major drawbacks in the use of this synthetic crystalline urea as a fertilizer were its hygroscopicity and presence of biuret in toxic levels. Because of high hygroscopicity, crystalline urea either straight or in mixtures with other fertilizer components, would become moist, cake on storage and have poor handling properties. This disadvantage has been overcome to a large extent by the production of prilled (pelleted) urea which has better storage and handling properties. Storage properties were also improved by packing it in moisture-proof bags. Urea with even better physical properties is now being prepared by coating the prills with an inert substances, like resin or elemental sulphur (Army 1963; Terman and Hunt 1964).

When urea is heated, two molecules condense with the elimination of ammonia to give biuret ($NH_2.CO.NH.CO.NH_2$).

$$2NH_2.CO\,NH_2 \longrightarrow NH_2.CO.NH.CO.NH_2 + NH_3$$

Thus during the manufacture of urea, the high temperature used for the reaction and processing gave rise to biuret as an impurity in the final product. The high amounts of biuret in the early urea preparations were found to cause injury to the plant:—since plants are unable to metabolize biuret, they tend to accumulate it (Impey and Jones 1960a). Recently new technological processes have been developed to produce urea of low biuret content ($<1\%$). These preparations can be used safely, on a variety of crops, even as a foliar spray.

The use of urea as a nitrogen fertilizer has increased tremendously in recent years, because of the above improvements in its production technology and due to its several other advantages, particularly its cheapness. The total world production of urea in 1954 was about 350,000 tons and estimated production in 1969 is 15,000,000 tons (Anon. 1966). Two other main uses of urea are in the plastic industry and in animal feeds.

Advantages of urea as a fertilizer

Urea is the cheapest form of nitrogen fertilizer presently available. This is at least partly due to its composition, which does not require a second compenent for its manufacture (cf. sulphuric acid is an expensive component required for the production of ammonium sulphate). Further, because urea has a high nitrogen content of 46%, transport and handling charges and possibly even application costs are low. Its properties also make it a suitable compound for foliar application. (This aspect is discussed under a separate section.)

Urea has yet another advantage. It does not acidify the soil to the same degree as some of the non-calcium containing nitrogenous fertilizers. For example, to neutralize the acidity caused by 10 lb nitrogen as ammonium sulphate, 54 lb of calcium carbonate is required, whereas only 18 lb calcium carbonate is required to neutralize the acidity caused by 10 lb nitrogen as urea (Anon. 1960). Hence in soils where acidification is a problem, the use of urea is definitely advantageous.

Fate of urea applied to the soil

There is some evidence that certain plants can absorb urea as such and assimilate it either after hydrolysis to ammonia and carbon dioxide or directly (Webster 1959). Evidence so far indicates that tea plant also takes up urea as such when large doses of urea are applied to the soil (Bhavanandan 1970). However, the major part of the urea applied to the soil is utilized by the plants after hydrolysis to ammonium carbonate.

$$H_2N.CO.NH_2 + 2H_20 \longrightarrow (NH_4)_2\,CO_3$$

This hydrolysis, which can be catalysed by acids and alkalis, appears to be catalysed in the soil mainly by an enzyme called urease (Conrad 1940). The source of this enzyme in the soil are micro-organisms (bacteria, actinomycetes and fungi) and crop residues. The rate and extent of hydrolysis of urea in the soil therefore depends on the microbiological activity of the soil, which in turn depends on factors such as fertility, soil temperature, soil pH, *etc.* The production of ammonium carbonate on hydrolysis causes a temporary increase in the soil pH. An increase in pH, particularly if it exceeds seven, may cause the release of one molecule of ammonia from ammonium carbonate with the formation of the more stable ammonium bicarbonate.

$$(NH_4)_2CO_3 \longrightarrow NH_4HCO_3 + NH_3$$

This release of ammonia has two disadvantages. Firstly, it can cause injury to germinating seeds and to emerging young plants. Secondly, it may volatalize into the air resulting in loss of nitrogen. The first problem has been overcome by separating the urea and seed by soil at planting (Widdowson and Penny 1963), or by mixing urea with acid material such as superphosphate before applying to the soil (Low and Piper 1961). In the case of tea, since only cuttings are used for propagation this problem does not arise. Foliar applications of urea (1–3%) have been successfully used in tea nurseries in Ceylon. Bhavanandan (1969) found that urea was as good as ammonium sulphate for application to young tea planted in the field.

The loss of nitrogen by volatilization can be prevented or at least reduced by mixing the urea with soil, by forking, or by placing it below the surface. The same results can also be obtained if the urea broadcast is washed into the soil by rain falling subsequently. Once the urea is below the surface of the soil, the ammonia released by hydrolysis would be absorbed and retained by the soil. The ability of the soil to absorb ammonium ions is determined, by its base exchange capacity (BEC). Thus losses would be greater from soils with low BEC, particularly sandy soils as compared to rich organic soils which have higher BEC (Gasser 1964). Other important factors determining volatilization loss of ammonia are soil pH and soil temperature. Both high pH and high temperature could lead to increased losses of ammonia by volatilization (Martin and Chapman 1951).

Nitrification of urea nitrogen

Nitrification is the microbiological process in the soil whereby ammonium ions are oxidized to nitrate ions. This process occurs in two stages; firstly ammonium is oxidized to nitrite by *Nitrosomonas* bacteria, followed by the oxidation of nitrite to nitrate by *Nitrobacter* bacteria

$$2NH_4^+ + 3O_2 \xrightarrow{\textit{Nitrosomonas}} 2NO_2^- + 2H_2O$$

$$2NO_2^- + O_2 \xrightarrow{\textit{Nitrobacter}} 2NO_3^-$$

Both these bacteria function well in soils with pH nearly neutral or slightly alkaline, 6.8—8.0, and the limiting acidity for the activity of these bacteria in the soil is around pH 4.0 (Waksman 1927). Normally the *Nitrobacter* is more active and therefore nitrate is oxidized to nitrate as fast as it is formed. If the soil pH is high (*c.* 8.5) then *Nitrosomonas* activity outstrips *Nitrobacter* activity resulting in the accumulation of nitrite (Campbell and Lees 1967). Nitrite is not assimilated by plants and is considered phytotoxic (Court *et al.* 1962).

In tea soils which are usually acidic, nitrification would be slow. When urea is applied to these soils, the initial hydrolysis to ammonium carbonate would result in an increase in pH (Bhavanandan 1970). This rise in pH, even though transitory, would favour the activity of nitrifying bacteria and increase nitrification. The possibility of the pH becoming very high (>8.5) and causing an accumulation of nitrite would be less likely in the highly acidic tea soils. But when urea is applied to soils with pH ranging from slightly acid to slightly alkaline, the possibility of nitrite accumulation is high. Accumulation of nitrite could lead to losses of gaseous nitrogen due to certain chemical reaction (Soulides and Clark 1958; Clark *et al.* 1960), in addition to being phytotoxic.

Movement of urea in the soil

When an ammonium salt is applied to the soil it would in the presence of moisture ionize to give positively charged ammonium ions. These ions would then be held rather firmly by the strong cation exchange sites present on soil colloids. Whereas the negatively charged nitrate (and nitrite) anions, formed either by ionization of nitrate salt applied to the soil or by nitrification of ammonium ions, would only be held feebly because the anion-exchange complexes of soils are relatively weak. As a consequence percolating rain water would leach out the weakly held nitrate and nitrite anions, but the strongly held ammonium cation is not liable to easy leaching.

As urea is a non-electrolyte, it does not dissociate into charged ions in solution. Naturally then it would not be held by either of the exchange complexes of the soil and as a result would be easily leached into deeper layers of soil. But (Broadbent *et al.* 1958; Bhavanandan 1969) showed that urea is not so easily leached and that it moves less rapidly than nitrate in soil. One reason for this unexpectedly low loss of nitrogen from urea by leaching is its rapid conversion to ammonium carbonate and the subsequent retention of ammonium. Various other reasons have also been suggested for this retention of urea by soil. Chin and Kroontje (1962) have suggested that urea forms an addition complex with organic matter of the soil and is therefore not easily leached out. According to Matsui, Namoika and Mukaï (1960) van der Waals forces and hydrogen bonding between urea and humus or clay are responsible for the retention. Broadbent *et al.* (1964) suggest that salt formation between the weakly basic urea and the weakly acidic groupings, like carboxyl of the soil, is responsible for urea retention.

The leachability of urea as compared to that of the ammonium ion has advantages in certain circumstances. When an ammonium fertilizer is applied to the soil by broadcast, as is usually done in fertilizing tea, most of the ammonium ions would be held in the upper layers (first few inches) of the soil. The plant can make use of this only by putting out feeder roots into the surface layers of the soil or after it is nitrified and the nitrate leached to the root zone. Whereas, when urea is applied by broadcast it can be reasonably expected that at least a part, depending on the rainfall, would be leached to the root zone before it is hydrolysed and retained as ammonium, thus discouraging surface rooting of the plant.

Use of urea as a foliar spray

Urea is highly soluble in water and is less corrosive than other fertilizer salts. It is therefore well suited for foliar spraying and also for application to soil as a solution, either by injection or in irrigation water. For foliar spraying, it is compatible with most insecticides, fungicides and salts such as zinc sulphate, epsom salt, *etc.*

Urea absorbed by the leaf is utilized after hydrolysis to ammonia and carbon dioxide by the urease present in the leaf (Hinsvarke *et al.* 1953; Dilley and Walker 1961). As foliar sprays urea solutions of very high concentrations can be phytotoxic due to localized production of large amounts of ammonia. Addition of a detergent, for example Teepol, prevents damage to the foliage to some extent. This is partly due to the film-forming action of the detergent which would prevent high concentration of urea in the form of drops. It is not known whether Teepol competes with urea for entry into the leaves and thereby reduce damage. Montelero *et al.* (1953) found that magnesium sulphate when added to urea spray solutions prevents damage to leaves by decreasing the amounts of urea absorbed. Sucrose is also reported to have similar effects as magnesium sulphate in preventing scorch.

It is, therefore, important to work out the safe concentration that can be used for the different crops. On tea, very little or no damage was noticed with urea concentrations up to 3% when sprayed at the rate of 100 gallons per acre (or 100 ml per plant). If Teepol was added to the spray solution then it was possible to increase the concentration of urea applied to 4% without serious damage to the leaves (Bhavanandan 1969). Absorption of urea is very much faster if urea is applied to the lower surface of the leaves (Impey and Jones 1960b; DNB *et al.* 1967; Bhavanandan 1970). It is reported that when applied to the lower surface 75—80% of the urea was absorbed in two hours by orange leaves. However, even when applied to the upper surface generally the absorption was complete in about 30 hours (Impey and Jones 1960b). Intensity of sunlight and temperature are other factors which could influence the rate and amount of absorption of foliar sprays. Urea foliar sprays have been successfully used on a variety of crops; for example, wheat (Finney *et al.* 1957), oranges (Labanauskas *et al.* 1963), apples (Oland 1963) and tea (Chiang 1960).

Field experiments with urea

Field experiments with urea as a fertilizer for crops have given mixed results. For certain crops (rice, potatoes, sugar beet, cotton) urea was found to be as good as other forms of nitrogen whereas for others (sugarcane, coffee, wheat) it was found to give slightly less yield than the other forms. For grasses, urea was found to be markedly inferior probably due to large losses of ammonia by volatilization. Generally for cereals and grasses where nitrogen is combine-drilled, urea decreased yield due to damage to germinating seeds and emerging seedlings. But when urea was worked into the seed bed before sowing it was as good as ammonium sulphate or calcium nitrate (Gasser 1964 and references cited therein). The rate of application of urea had a large influence on the results. Stephen and Waid (1963) found that at low rates or urea application 12 different crops gave similar yields with urea, ammonium sulphate and ammonium nitrate whether the fertilizer was top-dressed or base-dressed.

Most of the field experiments on urea have been carried out in temperate regions. Results of only a few experiments from the tropics are available. (For rice, urea is reported to be a good source of nitrogen in most parts of the world where this cereal is cultivated). The findings of Enyi (1965), working in Nigeria, are different from those of the workers in temperate regions. Enyi finds that urea was as effective as ammonium sulphate in increasing dry weight yield of maize, cotton, castor and pidgeon pea while sorghum gave lower yield with urea. The results were same for four different methods of application of nitrogen *viz.* base-dressing, top-dressing, split application and band placement. In a field experiment both forms of nitrogen gave similar yields with maize at all nitrogen levels tested. Further, no nitrite was detected in urea treated soils (cf. Court, Stephen and Waid 1962; Cooke 1962; Court, Stephen and Waid 1964).

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