SLOW RELEASE FERTILIZERS AND CITRUS: EMERGING FACTS

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ABSTRACT

Nutrient conservation by various means has been acquiring the status of core agenda in nutrition programme of citrus. Researches accrued worldwide in both pre-bearing and bearing orchards showed no unanimity in response over space and time. The results are, however, more encouraging in pre-bearing than bearing orchards. Many experimental evidences have strongly supported the reduced application frequency of fertilizers compared to conventional uncoated fertilizers. The slow release concept can very well be extended to nutrients other than N, e.g. phosphogypsum coated urea, micronutrients like frits, metal ammonium phosphate etc. with additional advantage of natural coating and chelating materials. Different longevity ratings of slow release fertilizers could well be synchronized with nutrient demand at various growth stages with nutrient release pattern, with uniform efficiency on both coarse as well as fine textured soils.

Concerns over energy conservation and ground water pollution, coupled with the competitive pressure to reduce production costs (Fairchild and Brown, 1986) have warranted ways and means to reduce the cost of applied fertilizers without affecting either fruit yield or quality. With the inception of intensive citriculture involving high density planting coupled with fertigation, nutrient conservation has assumed the status of core agenda on cultural practices on the pretext of heavy leaching losses of nutrients and subsequently, the growing intensity of ground water pollution. In this regard, the controlled release fertilizers including the polymer coated fertilizers offer a promising alternative. Different longevity ratings of slow release fertilizers could synchronize the nutrient demand at various growth stages with nutrient release pattern.

The importance of the controlled release concept in agriculture (Cardarelli, 1976), and particularly in fertilizer manufacture (Hays, 1971; Lunt, 1971), was reviewed long back. In the past, a number of reviews focusing the common controlled release concepts and materials have been put forward by many researchers (Hauck and Koshino, 1971; Prasad et al., 1971; Hauck, 1972; Davies, 1976; 1988). Nitrogen is the most important nutrient element in the citrus fertilization program (Dasberg et al., 1984). The frequent applications are, thus, recommended to ensure that there is a continuous supply for optimum plant growth and fruit production (Koo et al., 1984). Slow-release nitrogen sources were also effective in reducing the amount of nitrogen lost through leaching (Khalaf, 1980). These sources increased fruit production on mature citrus (Koo, 1986) and growth of young containerized citrus (Fucik, 1974; Khalaf and Koo, 1983) compared to soluble fertilizer sources.

Controlled-release fertilizers potentially reduce N losses and improve efficiency of plant recovery (Khalaf and Koo, 1983; Okada et al., 1992). Since a fewer applications are needed (Maynard and Lorenz, 1980; Jackson and Davies, 1984; Koo, 1986; Yuda et al., 1987), which reduce labour, equipment costs, and soil compaction produced through tillage operation. Controlled-release fertilizers have been used on many horticultural crops (Maynard and Lorenz, 1980), including citrus. Slow-release fertilizers produced more growth of very young citrus trees than more soluble sources (Fucik, 1974; Khalaf, 1980), probably due to a continuous rather than a fluctuating supply of nutrients. In contrast, growth of young Orlando tangelo trees was comparable

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for controlled release sulfur coated urea and soluble sources, but the frequency of application was reduced by 50% (Khalaf and Koo, 1983; Jackson and Davies, 1984).

Nakama (1967) presented the estimated amounts of nitrogen absorption in a year by calculating the difference of nitrogen contents among some trees which were different in tree age. Other studies (Hirobe and Oogaki, 1969; Kato et al. 1981) indicated that the nitrogen absorption during summer season is attained up to 50% to 70% of total absorption in a year for 'Satsuma' mandarin trees. Timing and placement of fertilizer application to coincide with peak periods of utilization is foremost in importance as an aid in this endeavour.

Potential Benefits

Usually, the release of nutrients is marked by high nutrient release at the beginning when plants are comparatively small and nutrient requirement is lower, and at later stages, the release is far slower. The potential benefits of controlled release fertilizers can be listed as i. greater efficiency of coated fertilizer source than with soluble fertilizers, i.e. nutrient availability extends over a long time period, ii. decreased leaching, since the availability is more attached to plant removal; iii. risk of toxicity or burning from a single large application of soluble fertilizers; and iv. long lasting effect due to continuous supply (Patel and Sharma, 1977; Maynard and Lorenz, 1980).

The balance sheet of soil N is an indication about the transformation which the controlled release fertilizer undergoes. Number of studies in the past have addressed the N nutritional problems by focusing the leaching losses from different controlled release fertilizers (Alva, 1992; Cox 1993; Wang and Alva, 1996; Paramasivam and Alva, 1997) and their biometric response (Koo, 1983; Obreza, 1990; Obreza and Rouse, 1991). The use of controlled-release fertilizers led to reduced rates and number of applications during the growing season (Jackson and Davies, 1984; Zekri and Koo, 1991) that could bring about substantial labour and time savings.

Mechanisms of Loss and Control

The urea applied to soil is rapidly hydrolyzed to ammonia by urease enzyme and due to its high local concentration, ammonia evaporates into the atmosphere at a rapid rate. Volatilization loss of ammonia is the major source of N loss from urea. Other losses include nitrification of ammonia to form nitrate ion which rapidly leach away from the root zones and denitrification which converts nitrate to elemental nitrogen under anaerobic conditions in the soil (Mishra and Khan, 1985). The N losses from the soil can be controlled through various methods. These include: i. coating of soluble fertilizer with insoluble materials thereby reducing its solubility and release into the soil, ii. chemically converting the fertilizer into less soluble forms, iii. by incorporating urease and nitrification inhibitors which will control the chemical transformation (Ayyer, 1992). The process of release of nutrients from coated fertilizers is dominantly governed by diffusion (Friedman and Mualem, 1994).

Among the chemically converted less soluble forms of N fertilizers, urea aldehyde condensation products have proved to be of importance in controlling N losses by their reduced solubility as well as slower microbial degradation. The products commercialized in this category are: i. ureaformaldehyde condensation products known generically as ureaform which is a mixture of low molecular weight methylene ureas, ii. urea-isobutylaldehyde reaction product which is a single product known as isobutylidene diurea (IBDU) manufactured by Mitsubishi by dry process and BASF by wet process, having nitrogen content of 31% and iii. crotonylidene diurea (CDU), a cyclic condensation product of acetaldehyde and urea (Hauck and Koshino, 1971).
The incorporation of specific chemicals which can regulate the microbial mineralization of urea has also been investigated at length. Phenyl phosphorodiamidate is a urease inhibitor and found to be promising, though subsequent work showed that it decomposes to phenol in the presence of urea. The nitrification inhibitors have gained much importance and several products are commercially available. These include N-serve, terrazole and dicyandiamide (Prasad et al., 1971). Due to their low melting and boiling points, N-serve and terrazole have found application mainly in liquid fertilizers. Some quantitative models have been suggested to describe the phenomenon of release of nutrients from coated fertilizers which are by and large affected by various factors like soil organic matter, moisture supply, pH and microbial activity (Kochba et al., 1990; Hassan et al., 1992; Shiviv and Mikkelsen, 1993).

**Controlled Release Materials**

In the past, waxes, polymers and sulfur have been primarily used as coatings (Powell, 1968). The slow or controlled release of fertilizer nutrients over a period of time may result from chemical, physical, or biological differences among the materials. The ways in which release rates can be controlled are: i. the application solubility coatings to soluble fertilizers, ii. the manufacture of compounds with low solubility, compounds which in addition require microbial activity for release of the nutrient. These are treated as natural organic materials, and require microbial action for release of nutrients.

A number of reviews focusing the common controlled release concepts and materials have been put forward by many studies in the past (Hauck and Koshino, 1971; Prasad et al., 1971; Hauck, 1972; and Davies, 1976; Mayanard and Lorenz, 1980 and recently by Carbera, 1997 and Rouse 2000). Release of nutrients from coated fertilizers is affected by nature and properties of coated materials, which may be either thermoplastic resin or additives as surfactants. The review of literature on use of urea supergranule reveals its effectiveness under waterlogged conditions to contain losses through excess leaching and denitrification. Citrus being an irrigated perennial crop hold comparatively less promise due to its higher vulnerability towards higher volatilization loss of N.

**Coated Soluble Materials** : Urea, because of its high analysis, good physical properties and relatively low cost, is the major source of nitrogenous fertilizer throughout the world. Coating materials for soluble fertilizers must be thin to avoid excessive dilution of the fertilizer and must be uniform and free of imperfections to avoid rapid and excessive dissolution (Slack, 1968). The only coatings of those studied which provide these characteristics together with acceptable cost are sulfur, certain waxes, or various polymers (Hauck, 1972). Sulfur coating of urea and polymer coating of soluble fertilizers (Osmocote process) are the most notable examples of coated fertilizers.

**Table 1.** Characteristic features of various types coating material and their effectiveness.

<table>
<thead>
<tr>
<th>Coating material</th>
<th>Nutrients supplied</th>
<th>Effectiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCU</td>
<td>N, S</td>
<td>Variable approximately per cent/day</td>
</tr>
<tr>
<td>Osmocote</td>
<td>N, PK</td>
<td>3 to 4 months, 8 to 9 months</td>
</tr>
<tr>
<td>IBDU</td>
<td>N</td>
<td>55% in 21 weeks for 1.0 to 1.2 mm particles</td>
</tr>
<tr>
<td>CDU</td>
<td>N</td>
<td>31% in 10 weeks</td>
</tr>
<tr>
<td>Triazines</td>
<td>N</td>
<td>10% for 15 weeks</td>
</tr>
<tr>
<td>MagAmp</td>
<td>N, P, Mg</td>
<td>100 days for incorporated coarse granules</td>
</tr>
<tr>
<td>Gypsum</td>
<td>N, Ca, S</td>
<td>3 to 4 months</td>
</tr>
<tr>
<td>Ureaform</td>
<td>N</td>
<td>60% in 6 months for 75% insoluble material</td>
</tr>
<tr>
<td>Activated sludge (Milor granite)</td>
<td>N, P, K</td>
<td>2-4 material</td>
</tr>
<tr>
<td>Ammelide</td>
<td>N, P, K</td>
<td>35 per cent in 7 days at 31°C± 1.5°C</td>
</tr>
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</table>

SCU, IBU, and CDU stand for sulfur coated urea, isobutylidene urea, and crotonylidene diurea, respectively.
Source: Maynard and Lorenz (1990); Sharma (1979); Rutten (1980); Cabrera (1997). Controlled-release fertilizers have proved very promising for sandy soils and subtropical environments as they can be applied in smaller amounts and less often than soluble fertilizers, without adverse effects on tree growth or fruit production and quality (Zekri and Koo, 1992). Reduced weight per fruit from the soluble fertilizer treatment could have been caused by reduced K in the leaves (Reese and Koo, 1975). In another study, Zekri and Koo (1991) found that individual fruit weight increased with controlled-release fertilizers as compared with soluble sources. The lack of differences in other fruit quality characteristics and fruit yield would be attributed to high variability in the first year of fruiting. Soluble fertilizers produced smaller size fruit and yielded less fruits than controlled-release fertilizers, but the differences in fruit yield were not significant (Cabrea 1997). Controlled-release fertilizers have been tested on citrus for only a few years (Khalaf and Koo, 1983; Jackson and Davies, 1984; Marler et al., 1987; Ferguson et al., 1988). Most of these studies conducted on young trees were short-term experiments focused mainly on the effect of several controlled-release fertilizer sources on tree growth.

**Sulfur-coated urea (SCU):** Sulfur coatings alone have numerous imperfections which require an additional wax sealant to control dissolution (Anonymous, 1974; McClellan and Scheib, 1973; Scheib and McClellan, 1976). The thickness of the S-coating (Oertli, 1974) also influences dissolution. The general properties and applications of SCU are well documented (Allen et al., 1968; Allen and Mays, 1971; Porter, 1971; Davies, 1976; Lunt, 1967). The final composition of SCU varies with coating weight; however, a typical product contains about 36% N, 17% S, 3% wax, 0.2% micro biocide, and 1.8% conditioner.

Controlled-release sources of nitrogen were compared by Koo (1986) with a soluble source on bearing citrus where increased fruit production of Pineapple orange was found with controlled-release sources of N over the soluble source in both experiments without any difference in fruit quality. Combining soluble and controlled-release fertilizers in a plant nutrition programme offers an economical and effective strategy for citrus growers (Zekri and Koo, 1991).

**Polymer coated fertilizer:** The most widely used controlled fertilizers in container nursery plant production are polymer-coated fertilizers. The polymer coated fertilizers consist of soluble fertilizers encapsulated in a polymer coating. Each fertilizer capsule is called a prill. Polymer coated fertilizers which release nutrients through a semi-permeable membrane formed by the polymer coating and water vapour diffuses into the prill which condenses, and then dissolves some of the fertilizer salts inside the prill, thus, the resulting fertilizers solution thought to be released either via diffusion (Bunt, 1988; Geortz, 1993) or the forcing of nutrients solution out of membrane by hydrostatic pressure (Kochba et al., 1990; Oertli, 1980).

In trials on ‘Satsuma’ mandarin (Citrus reticulata) grown with 6 or 12 g N/pot as slow release fertilizers nitricote 100, Nuricote 180 or sodium nitrate in April, June, and August were applied. With Nutricote 100 or Nutricote 180, the shoot growth, shoot pruning weight and trunk diameter increase were greater than with only other fertilizer except that shoot growth. The higher rate of N as ammonium sulphate was comparable to that with Nutricote. Return bloom in late April was 192.3 and 167.6 for Nutricote 100 and 180 at lower rate compared with 12 for cyclourea at lower rate, 9.8 for cyclo-urea at higher rate and 16.4 for sodium nitrate at higher rate (Yuda et al., 1987). Lamont et al. (1987) observed similar pattern of nutrient release from osmocote versus...
A 4-year old study was conducted to compare 2 rates of controlled-release fertilizer application with conventional granular soluble fertilizer for mature grapefruit cv. 'Marsh' trees on sour orange rootstock. Annual NPK application in spring, consisted of 20-3-17 Osmocote at 20 kg/ha or 36 kg/ha. The 10-4-12 granular fertilizer was applied as equal split applications in April or May and October or November to provide a total of 134 kg N/ha.

Leaf analysis showed higher N contents for the conventionally manured plots in 2 of the 4 years. Only minor differences were noted in juice quality parameters and fruit yields between treatments, despite the large difference in the quality of N applied (Boman, 1994).

Among the CRF products, longevity of nutrient release was significantly greater for the meister and osmocote compared with poly-S (Paramasivam and Alva, 1997). Ranking of the various N sources, with respect to total N uptake by the seedlings was: meister = osmocote > poly-S > urea > no N for Cleopatra mandarin rootstock, and meister = poly-S = osmocote > urea > no N for citrumelo rootstock. For a given rate of N application the total N uptake by seedlings was greater from CRF than from urea. This suggested that various N losses were lower from the CRF than from soluble fertilizers (Dou and Alva, 1998).

The potential for minimizing leaching loss of nitrate-N was evaluated by Alva and Tucker (1994) in a replanted old citrus grove on a typical deep sandy soil. An increased rate in nitrate-N loss through leaching was evident when using dry soluble fertilizer compared with controlled-release fertilizer, as indicated by the concentrations in leachate sample at 5 ft. below ground level under the tree. Response of 'Hamlin' (Citrus sinensis (L) Osbeck) on cleopatra mandarin (Citrus reticulata Blanco) to application of polymer coated urea at the rate of 56, 112, and 168 kg N/ha./year in a Typic Quartzipsamment by Alva and Paramasivam (1998) showed an increase in fruit yield from 66 to 84 Mg/ha, 27 to 36 Mg/ha and from 68 to 85 Mg/ha with 56, 112, and 168 kg N/ha/year, respectively. The N requirements for 1 Mg of fruit, mean across all N rates were 1.79, 2.58, and 2.75 kg N for the polymer coated urea, fertigation, and dry granular form of NH4NO3. The leaf N concentration was maintained within optimum regardless of source and method of application.

**Low Solubility Materials**

The dissolution rate of compounds having low water solubility is closely related to the exposed surface area of particle. Hauck (1972) illustrates this point by comparing two particles of the same material that differ in size and density. The material in the two particles does not differ in solubility but does differ in dissolution rate because the larger, harder particles have a smaller surface volume ratio and will take longer to dissolve.

**Isobutylidene diurea (IBDU):** This compound is the reaction product of urea and isobutylaldehyde usually in 2:1 mole ratio. Theoretically, it contains 32.2 per cent N, but fertilizer grades contain about 30% N. The grades of mixed fertilizers are 15-15-15, 16-10-14, 18-11-11, 20-12-12, and 10-10-10, with the first four grades used widely in horticultural crops. The solubility of IBDU in water is initially very low at room temperature but hydrolysis occurs rapidly once dissolution begins. The rate of hydrolysis is not stable but is greater under acid conditions and at higher temperature (Hauck, 1972; Hauck and Koshino, 1971; and Prasad et al., 1971).

Crotonylidene diurea (CDU) is another such type of slow release N fertilizer containing 31% nitrogen. Sannigrahi (1996) showed that application of IBDU and CDU observed maximum population of bacteria (125 x 10^3/g soil and 145 x 10^3/g, respectively), ammonifiers (79 x 10^3/g soil and 84 x 10^3/g...
soil), and actinomycetes (63 x 10^5/g soil and 62 x 10^5/g soil) compared to bacterial population (108 x 10^3/g soil), ammonifiers (60 x 10^3/g soil), and actinomycetes (69 x 10^5/g soil) with urea alone in a sandy clay loam Haplaquent soil type (pH 8.3, organic C 7.9 g/kg, at 80% water holding capacity, total N 0.8 g/kg, and CEC 15 cmol (P+)/kg).

Khalaf and Koo (1983) found less than 1% of applied N in the drainage water collected from the pots treated with IBDU and SCU compared with 22% for those treated with NH_4NO_3. Overall, the controlled-release N plots contained 23% more total N than the soluble N plots in the top 30 cm of soil (< 0.05). With mature citrus trees, Koo (1986) found that trees fertilized with IBDU yielded more fruit than trees fertilized with either SCU or NH_4NO_3 but quality were more prominent. The treatment NH_4NO_3 produced fruits with a higher soluble solids concentration than IBDU and SCU. However, SCU was less effective than IBDU in terms of leaf N concentration and fruit yield.

**Biodegradable Materials of Low Solubility Ureaform:** The term ureaform as applied to solid urea-formaldehyde fertilizers was coined by Clark et al. (1994) having a product which is largely a mixture of low molecular weight methylene ureas of the general formula NH_2CO(NHCH2NHCO)nNH_2 where n is in the range of 1 to 8. The quantity and quality of cold water insoluble nitrogen determines the solubility of ureaform as fertilizer.

Of the several slow release N tested by Tavdgiridge (1979) urea plus formaldehyde at 100 g/tree produced the best results with regard to tree growth and fruit chemical composition in Western Georgia. In another study, Tavdgiridge (1989) observed that application of methylenediurea provided uniform N nutrition which aided in protein synthesis and carbohydrate accumulation in the leaves. Tavdgiride and Putkaradze (1991) observed a high level of urease activity in mandarin trees fertilized with a ureaform aldehyde fertilizer and recommended ureaform as one of the best fertilizer for citrus in humid subtropical conditions.

**Other Slow Release Products**
Guanuylurea produced from i. calcium cyanamide by acid treatment and ii. by hydrolyzing dicyandiamide in acid medium. The CDU (Crotonylidenediurea or 2-Oxo-4 methyl-6-ureidole hexahydoxy pyrimidine) is prepared from the reaction between crotonaldehyde and urea and has decomposition rate faster in coarse textured soils.

**Difurfurylidene triureid** (a condensation product of urea and furfural); glycoluril (product of reaction between urea and glyoxal in presence of HCl); triazims (produced when urea and ammonia react under heat and pressure) such as cyanuric acid, ammelide, ammeline, and melamine contain 32-66% N; metal ammonium phosphates (divalent atoms viz., Fe, Mn, Cu, Zn, Co, Mo form with ammonium phosphate) such as Mag-Amp analyzing 8-40-0-14 (Mg and recent one Mag-Amp with K having 7-40-6-12 Mg) and nitrogen enriched coal (to a lesser extent) are also used as slow release fertilizers (Prasad et al., 1971). But, using citrus as a test crop, little or literally no information is available to date.

**Processed Natural Organic Materials**
Natural organic materials are also used as controlled release nutrient sources, since the very beginning of agriculture. The dicyandiamide nitrification inhibitor improved the N fertilizer efficiency and decreased NO_3^- losses so as to minimize and economize the environmental risks that are inherent in irrigated production of citrus (Sharma et al. 1994).

The efficacy order of the nitrification retarders in conserving NH_4^-N was nitrapyrin(NP) > neem oil(NO) > acetone extract of neem oil (ANO) > neem cake (NC) > ether extract of neem oil (ENO) > petroleum.
ether extract of neem oil (PNO) up to 30 days of incubation and the order change to NP = NO > ANO > NC > ENO = PNO at 45 days (Patel et al. 1995). Serna et al. (2000) observed that 3,4-dimethylpyrazole phosphate nitrification improved N fertilizer efficiency and reduced NO₃⁻ leaching by retaining the applied N in the ammonical form. Verma and Dashora (2000) reported that pre-harvest application of neem blended fertilizers reduced the post-harvest rotting of Kagzi limes (Citrus aurantifolia Swingle).

Glasscock et al. (1995) observed that nitrification inhibitory effects of two inhibitors viz, dicyandiamide and N-serve was enhanced at 200 and 400 mg/kg NH₄⁺-N addition in three soil types viz, clay, clay loam and sandy loam irrespective of the salt concentration.

**Nimin coated urea**: Nimin is a product derived from neem (Azadirachta indica). Bains et al. (1971) were the first to discover the role of neem in improving the efficiency of applied urea. Nitrification inhibitory property of neem was highlighted by a number of workers (Mishra et al., 1975; Chhonkar and Mishra, 1978; Tiwari, 1989; Suri, 1995; Suri et al., 1998; 2000). Coating urea with neem cake has helped in reducing volatization (Singh and Singh, 1984; 1986) as well as leaching losses (Subbiah and Kothandaraman, 1989). According to Bringi (1987), neem bitters (teraoctipenoids) reported to be responsible for nitrification inhibition, namely, nimbin, nimbinin, nimbidin, nimbinini, etc. are lipid associated constituting 2% of oil.

A concentrated neem extract which contains as much as 5% neem bitters responsible for nitrification inhibition in soils, has been prepared by processing industrial grade oil. Vyas et al. (1991) described the method of preparing neem coated urea. For this purpose, neem is repeatedly treated in order to remove the major part of triglycerides and free fatty acids. The resultant fraction is subsequently solvent extracted to concentrate the desired alkaloids. The extract has been named as nimin, which is a salt adhesive. Sharma and Sharma (1996) in their review highlighted the role of neem in horticulture from various angles.

**Future Line of Research**

The concept of slow release fertilizers in the past few years has gained a wide field application including the citrus orchards. The growth of citrus trees is cyclic in nature, therefore, a regulated supply of all essential nutrients is necessary to synchronise the supply with the nutrient demand, and sustain the high orchard productivity on a long term basis. To establish this fact, a long term integrated study is required to ascertain, how these coated fertilizers influence the available pool of nutrients vis-à-vis fruit yield and quality in comparison to conventionally uncoated fertilizers. Simultaneously, study on nutrient release pattern will substantiate to develop a crop log data so that same can be eventually fitted into the fertilization schedule of crop, especially on soils where percolation and leaching losses are of high magnitude.

Currently, the major efforts focus on nutrients like nitrogen. The same concept can be expanded to other nutrients like K, Fe, Zn, B etc. The occurrence of large scale multiple nutrient deficiencies in the recent past in citrus orchards has posed quite a challenge to the researchers to find an alternative means to conventional high analysis fertilizers to combat such problems. Pre-enrichment of a variety of organic manures could be on such option which requires sound data support in which nutrient release is mandatory to establish cause and effect relationship.

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