FORMULATION OF SPRAYS TO IMPROVE THE EFFICACY OF FOLIAR FERTILISERS

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ABSTRACT

Spray adjuvants can be employed in the foliar application of fertiliser to ensure adhesion of aqueous sprays to the waxy surfaces of foliage (wetters), to improve coverage of spray on foliage (spreaders), to minimise weathering of fertiliser deposits on foliage (stickers/extenders), and to increase the uptake of fertiliser into foliage (humectants, pH modifiers, and penetrants). Even with improved formulations using effective adjuvants, foliar fertilisers must be regarded as supplements to overcome deficiencies in micronutrients, and to boost macronutrients at critical physiological stages, rather than as substitutes for soil-applied fertilisers.

Keywords: nutrients; fertilisers; foliage; formulations; surfactants.

INTRODUCTION

The application of fertilisers to foliage has long been practised (cf. review by Swietlik & Faust 1984), and is attractive because the direct supplementation of soil nutrients may be either inefficient or ineffective (Leece & Dirou 1979). Additionally, foliar fertiliser application enables directed timing of nutrient applications to coincide with critical stress events such as growth flushes, flowering, fruit-set (Weinbaum 1988). This is possible because, in general, responses to foliar nutrients are much more rapid than those to soil applications (Knight 1991). There are increasing concerns about contamination of ground water by fertilisers, and foliar applications assist in addressing this matter (Alexander & Schroeder 1987).

The dilemma of foliar fertiliser application is that the waxy cuticle, covering the surfaces of all plant foliage (Martin & Juniper 1970), is an effective barrier to the penetration of exogenous chemicals into the underlying tissues (Price 1982). Despite this, the majority of systemic pesticides, whether fungicides, growth regulators, herbicides, or insecticides, are successfully applied in sprays to the foliage of crops. Thus, it is apparent that many of the principles of formulation employed with foliar-applied systemic pesticides also may be used to advantage for foliar fertiliser application.

PATHWAYS OF FOLIAR UPTAKE

Cuticular Penetration

The structure and chemistry of the cuticle have been reviewed previously in the context of foliar fertiliser application (Chamel 1986). Cuticular penetration is a passive diffusive process, "powered" by the concentration gradient existing across the cuticle. This gradient is controlled not only by the concentration of fertiliser within the applied spray, but also by the form and distribution of the spray deposits on the foliar surfaces, which can be modified by formulation (*see below*). Indirectly, frequency of application is also a means of controlling the concentration gradient.

While the existence of polar pathways through the essentially lipophilic cuticle remains equivocal, it appears that, at the microscopic level, the penetration of nutrients may be preferential at, or perhaps effectively restricted to, certain areas of the cuticle (Franke 1986). However, this knowledge is of little value to the users of foliar fertilisers. The innate rate of absorption varies among nutrients, and has been reported to be: urea $N > K \approx Mg > Ca > Mn \approx Zn > Cl > P \approx S > Fe \approx Mo$ (Wittwer 1964). Because the molecular size of nutrients is unlikely to restrict their penetration through the cuticle (cf. molecular weights of systemic pesticides), their lipophilicity is presumed to be the major factor controlling cuticular penetration, as is the case with pesticides. Evidence for this has been provided by the study of Coker *et al.* (1987) which showed that nitrogen applied to *Pinus radiata* D.Don as urea was absorbed 10 times faster than nitrate-nitrogen and three times faster than ammonium-nitrogen. This suggests that foliar application of suitably lipophilic organic compounds containing nitrogen, phosphorus, and sulphur may give enhanced absorption of these nutrients. The value of this approach must be considered with regard to the effective dilution of the nutrient element within its molecular "carrier", the potential physiological side-effects of the organic carrier, and the ultimate catabolism of the carrier to release the element in a biochemically suitable form. Manipulation of the lipophilicity of mineral nutrients may also be achieved by chemical formulation in pseudo-organic form, i.e., salts of organic acids (Shafer & Reed 1986) and chelates (Ferrandon & Chamel 1988).

Stomatal Infiltration

Stomata provide a direct route of entry to the leaf interior. Although the cuticle extends into the substomatal cavities, fertiliser introduced into the intercellular air-spaces is made rainfast (Neumann & Prinz 1974a), and the large surface area and high-humidity environment within the leaf must facilitate the rapid movement of nutrients into the tissues.

The requirements for infiltration of spray solutions into stomatal pores have recently been reviewed, and this pathway has been investigated with regard to the foliar uptake of pesticides (Stevens *et al.* 1991). The results of this study are relevant here because infiltration is a purely physical process, and thus the chemical nature of a spray's active ingredient (a.i.), whether nutrient or pesticide, is largely irrelevant. The fundamental requirement for infiltration is a low surface tension (<25–30 mN/m), which can be provided only by certain surfactants, notably the organosilicones. These have been developed as a novel class of spray adjuvants on the basis of research at the New Zealand Forest Research Institute (Stevens 1993a). Indeed, it was early research on foliar fertiliser application to alleviate iron chlorosis in citrus, with addition of Silwet L-77 to sprays, that first highlighted the infiltration capability of the organosilicones (Neumann & Prinz 1974b).

Stomata can be an important pathway for the uptake of nutrients into the foliage of some species. However, the upper (adaxial) surface of foliage is the primary site of spray deposition and many broadleaved species have stomata only on the lower (abaxial) surfaces of their leaves, so that infiltration of spray solutions may be of limited importance. This has been illustrated by the failure of applications of iron with L-77 specifically to the astomatous upper (adaxial) leaf surface of orange to correct iron chlorosis, in contrast to the benefit of those made to the stomatous abaxial (lower) surface (Levy & Horesh 1984).

FORMULATION

Wetters/Spreaders

Surfactants (surface active agents), by virtue of their amphipathic nature (part watery, part oily), adsorb at the surface of spray droplets, effectively making the surface partially oily in nature so that it can wet the foliage (Stevens 1993b). Thus, droplets containing surfactant are more likely to adhere to waxy leaf surfaces, and can penetrate the mat of hairs overlying the surface of the leaf of some species to bring the nutrient into direct contact with the leaf surface.

Surfactants also spread the droplets out, providing a greater contact area for uptake of nutrient. Wetting and spreading are distinct but very closely related properties, wetting being a prerequisite for spreading. Thus, all spreaders are, by definition, wetters but the converse is not always true. This is illustrated by the contrast between "conventional" surfactants and the organosilicone spray adjuvants (cf. stomatal infiltration), which are "super-spreaders". As a result, the use of high concentrations of organosilicones, in particular, in combination with high spray volumes may be counter-productive, because droplets may coalesce and subsequently run-off from foliage. It has been reported that on addition of L-77 (1 g/*l*) the volume of nutrient solution retained on the foliage of prune trees sprayed to run-off was halved (Weinbaum & Neumann 1977). An enhancement by L-77 of calcium levels in apple fruit was lost when the concentration of the organosilicone in the 2000 *l*/ha sprays, applied throughout the season, was increased from 0.5 to 1 g/*l*. The benefit of the L-77 was reinstated using the higher concentration when the volume rate was decreased to 1000 *l*/ha, clearly indicating that the high-volume, high-concentration combination was resulting in run-off (Stevens & Zabkiewicz 1990).

Stickers/Extenders

These adjuvants are used to prolong the life of nutrient deposits on foliage, primarily by reducing their wash-off by rain. Stickers/extenders work by forming a polymeric, plastic-like deposit on foliage, in which the nutrient is entrapped. This has the additional benefit of providing a humid micro-environment within the nutrient deposit which is likely to facilitate uptake into the plant (cf. humectants).

Stickers/extenders may be supplied as polymers; examples of these adjuvants are Latron B-1956 (formerly Triton B-1956: Rohm & Haas) which is a resin dissolved in a solvent, and

Bond (Loveland), a latex-based product. Various other stickers/extenders are based on menthene, which reacts in the presence of sunlight to form a polymer on the leaf surface.

Humectants

Humectants are hygroscopic and thus retain water within the visibly dry deposit on the leaf surface, maintaining the nutrient partially in solution and facilitating its uptake. Although distinct, humectants are commonly confused with anti-evaporants. This is understandable, because prolonging the drying time of spray droplets can be expected to have a similar effect; uptake into foliage was 100- to 1000-fold faster from freshly applied spray droplets than from their resulting dried deposits (Stevens *et al.* 1988).

Some nutrient salts are themselves highly hygroscopic, e.g. magnesium chloride which, presumably for this reason, is taken up more rapidly than the much less hygroscopic magnesium sulphate (Allen 1970). Surfactants are humectants to varying extents, and foliar uptake has been correlated with the water retention by an homologous series of surfactants (Stevens & Bukovac 1987). Glycerol is probably the humectant which has been most commonly employed; it has, for instance, been demonstrated to be beneficial for the application of urea to prune (Leece & Dirou 1979).

pH

pH affects the ionic status of some nutrients, and also that of the cuticle because it contains some free (unesterified) carboxylic acids (Holloway 1982), and incorporates embedded waxes which are principally fatty acids (Baker 1982). Various nutrients may therefore display a pH dependence for their uptake into foliage, and the optimum pH range for the uptake of phosphate has been shown to vary with the chemical nature of the counterion (Reed & Tukey 1978). LI-700 (Loveland) is a spray adjuvant comprising acidified soy phospholipid, which has been shown to be beneficial with manganese, e.g., into barley (Dawson 1992). Whether this is attributable solely to pH, or also to other properties of the adjuvant, is uncertain.

Penetrants

Cuticular

Surfactants can enhance cuticular penetration, but this process is not yet fully understood. It is clear that the combination of surfactant/penetrant/plant is highly specific, and it has only recently become possible to generalise and make some recommendations on a physical-chemical basis (Holloway & Stock 1990). Only one, extensive, systematic investigation of surfactants appears to have been conducted with respect to foliar nutrient (iron) absorption (Nelson & Garlich 1969) and, not surprisingly, the effects of ionic surfactants appeared to be highly specific to their class (phosphates > sulphonates ≈ amines > sulphates ≈ amides ≈ quaternary ammoniums). In contrast, with nonionic surfactants a clear trend was established across chemical classes with those of high HLB (hydrophile:lipophile balance), i.e., the most polar surfactants, being the most effective. While the effects of the ionic surfactants could probably be associated largely with their counterionic behaviour, it is not clear whether that of the nonionic surfactants was attributable to penetrant or humectant properties (q.v.).

In addition to surfactants, various other chemicals have been employed as penetrants. Arguably, glycerol (cf. humectants) has some penetrant properties. Dimethyl sulfoxide (DMSO) is a solvent which has been shown to increase the uptake of some nutrients (Chamel 1988).

Stomatal

Silwet L-77 is sold as an agrochemical adjuvant in New Zealand under the tradename Pulse (Monsanto), and is advertised as a penetrant because of its ability to induce infiltration of stomata. Various other organosilicones and organosilicone-based adjuvants are available in other countries and, in addition to L-77, Boost (DowElanco) and Freeway (Nufarm) are marketed in New Zealand. Infiltration has been shown to be effective with numerous combinations of nutrients and crops in addition to iron on citrus, e.g., potassium nitrate on prune (Weinbaum & Neumann 1977), and magnesium and phosphate on potato (Rimmer & Green 1992).

Copenetrants

It is well established that chemicals will commonly affect the foliar uptake of one another. This is most apparent as the effect of the counterion on the uptake of nutrients (Cook & Duncan 1983; McPhail & Duncan 1989). There is considerable logistic, and thus economic advantage in mixing spray chemicals for simultaneous application; however, this raises the potential problem of compatibility (Sander *et al.* 1987), and the presence of nutrient salts has been shown to modify the activity of various herbicides (Wills & McWhorter 1985).

PHYSIOLOGICAL CONSIDERATIONS

Phytotoxicity

Application of concentrated solutions of foliar fertilisers may locally scorch the leaf tissue. Osmotic shock is often implicated although there are innate differences among fertilisers (Neumann 1988). "A little and often" would therefore be a good discipline to minimise the risk of phytotoxicity, while restoring the concentration gradient for cuticular penetration (q.v.) and thus maximising uptake. Logistically, however, this is not a desirable policy, and so spreaders may be used to effectively dilute the deposit on the foliage. Thus, reduced phytotoxicity of iron sprays to citrus was observed with addition of L-77 (Neumann & Prinz 1975). Nonetheless, surfactants must be employed with discretion, because surfactants are themselves potential phytotoxicants (Coupland *et al.* 1989), and because too great an increase in the rate of nutrient uptake is likely to reinstate phytotoxic damage. The latter is most likely when the stomata are infiltrated (Weinbaum & Neumann 1977).

Translocation

Nutrients may require redistribution within the plant, from their sites of absorption to those tissues where they are required. There are innate differences in the mobility of nutrients, and they have been broadly classified by Bukovac & Wittwer (1957) as mobile (rubidium, sodium, potassium, phosphorus, chlorine, sulphur), partially mobile (zinc, copper, manganese, iron, molybdenum) and immobile (calcium, strontium, barium). There is evidence that surfactants inhibit basipetal translocation in the phloem (Coupland 1989). Nonetheless, reductions in the efficiency of translocation are commonly more than compensated for by increases in absorption afforded by surfactants. There may be an additional advantage when stomatal infiltration occurs, because nutrients are likely to be brought directly into close proximity with the vascular tissues. Such increases in nutrient export have been observed when L-77 was incorporated in the spray solution (Weinbaum & Neumann 1977).

CONCLUSION

The principles of spray formulation, which have mostly been developed for, and derived from, the use of systemic pesticides, can be employed to advantage with foliar fertilisers. Even with improved formulations using effective adjuvants, foliar fertilisers must be regarded as supplements to overcome deficiencies in micronutrients, and to boost macronutrients at critical physiological stages, rather than as substitutes for soil-applied fertilisers.

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