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Controlled Release Technologies: Applications in Tropical Agriculture (**)

ABSTRACT. — The concept of controlled release, minimizing the concentration of available active agent in the environment, is defined. This is based on reducing the losses of applied chemical and increasing its efficiency in use. Other benefits include extended control periods, safer formulations of hazardous substances, more selectivity and improving the potential of new labile compounds and microbial pesticides. Formulation types for use in tropical agriculture are described and potential areas for application and the benefits in relation to a "second green revolution" are discussed.

INTRODUCTION

Controlled release can be defined as the permeation-moderated availability of an active agent from a formulation to a target site over a specified period. This definition can include various release rate profiles such as a slow continuous or even rapid release, and encompasses the concept of a release rate appropriate to the requirements over time of an effective concentration at the target, with a knowledge of the delivery pathways and losses involved (Kydonieus, 1980).

Such principles of availability are similar to those used by living organisms in delivering regulating substances within their own tissues (Wilkins, 1982). In a similar way the use of defensive substances by plants, animals and micro-organisms against pathogens, predators and parasites is based on controlled release methods. The active agent may be released slowly or when needed, generated from precursors by the stimulus of the attacking organism (e.g., phytoalexins or protease inhibitors in certain plants). In fact, many conventional pesticides (Marini-

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Bettòlo, 1977) have been derived from plants and a further step in improving their use may lie in exploiting similar delivery systems as exist in nature.

In considering the role of future pest control agents in the coming second green revolution, a gradual change (green evolution?) could be more appropriate. "Conventional" pesticides will continue to have an important and crucial position while newer biorational materials will be gradually introduced, as they are proven to be field effective. Controlled release technology can offer improvements in the use of the conventional pesticides as well as facilitate the performance, and thus introduction, of the new classes of pest control agents. Thus by emulating plants in this respect, the introduction of biological controls will be made that much easier. Biotechnology may have a place here in the production of new active agents, new microbials and also in the development of biodegradable polymers for formulation purposes with better release kinetics.

In considering the application of controlled release (CR) technologies to tropical agriculture, the actual mode of action of the active agent is less important that other factors. Thus, the active agent could be a nutrient, "conventional" pesticide, an attractant (e.g., pheromone or food bait), a hormone, an antibiotic or a micro-organism. The principles of controlled release remain the same for all active agents delivered and the potential benefits will depend on use factors (e.g., efficacy/efficiency, environmental and toxicological). The theoretical background supporting the use of CR and the potential benefits in tropical agriculture are discussed in the following sections.

Principles of Controlled Release in the Tropical Environment

All pest control agents, and fortunately most organic materials, both natural and synthetic, decompose at characteristic rates under various environmental conditions. For plant and animal protection the persistence of the active agent at the target is of crucial importance. Many environmental factors effect persistence including drift and run-off (during application) and degradation by light and micro-organisms, leaching, adsorption, evaporation and diffusion away (subsequent to application). All of these loss mechanisms reduce the available active agent, at a rate often dependent on its concentration, which defines its half-life (Hartley and Graham-Bryce, 1980). The losses are greatest for materials of short half-lives, and to obtain reasonable periods of control from such materials requires the application of high dosages. In this respect, the persistent organochlorine pesticides are very efficient, suffering small losses from the original concentration applied.

For short-lived materials the application needs to provide a reservoir which will maintain a minimum dosage at the target. The time scale can vary according to the specific situation, from hours to years. If this minimum concentration at the target could be maintained from a source without increasing the amount freely available, then the losses (which now depend on this minimum concentration) could also be minimized. Making this assumption, these minimal losses can be calculated (Allan *et al.*, 1973). For a pesticide with a short half-life of 15 days a typical comparison would be:

Duration of control required (days)	Amount needed conventional application (g/ha)	Amount needed continuous delivery (g/ha)
50	10	3.3
100	100	5.6
150	1000	7.9

It can be seen that the increase in efficiency becomes greater for longer periods of control. The corollary is that for shorter half-lives the efficiency gain is also high, for a fixed period of control. Under most tropical agricultural conditions, where temperatures are higher than for temperate zones, the half-lives and effective persistencies of pesticides are curtailed. Thus, the possible benefits, in terms of efficiency, from the introduction of CR to the tropics could be enormous.

Other Benefits Relevant to Tropical Agriculture

The principal objective of CR is to reduce ambient concentrations and thus, losses. Expressed in a different way this means that a fixed amount of an active agent will be effective for longer periods and this is needed for very short-lived materials such as pheromones and other insect behaviour-modifying chemicals for use in the open environment. Developments in CR technology have permitted this group of active agents to have a future in crop protection. Other short-lived insecticides, such as the juvenoid hormones, have been introduced to the market in a CR form (e.g., methoprene as Altosid 10SR), although mainly for non-agricultural applications.

Increased efficiency also means that less active agents could produce the same effect (i.e., crop yields) as compared to conventional formulations. This has been demonstrated for certain pesticides under tropical conditions (see below).

In some cases dramatic improvements in selectivity (i.e., to crop plants, non-target organisms or human operators) are produced by using CR technology. This can be the main motive for commercial usage (as in certain uses with the microencapsulated methyl parathion) (see Kydonieus, 1980). Selectivity between crop and weeds can be improved (see below). In the case of toxic pesticides, then the CR formulation with reduced access to the toxicant increases the safety to the operators, handlers and the general public. This could be of great importance in the tropics, where lack of awareness of the hazards of toxic materials has led to many accidents. Special formulations, particularly solid ones, reduce the potential for abuse, when the pesticide may be used for non-recommended, non-agricultural, uses.

Types of Controlled Release Technologies in Agriculture

Controlled release implies a formulation that can protect and release with a mechanism aimed to provide the optimum amount available at the target over a period. This usually involves polymers, and the release kinetics are dependent on the microenvironment of the device. Formulation types are normally divided into chemical or physical. Within the economic restraints of agriculture, particularly in the tropics, the more costly chemically-bonded pesticides are too expensive. An additional constraint is the extra cost of registration, in view of the fact that the US E.P.A. considers this type to be a novel molecule, although in the bound form it possesses no biological activity. With the exception of systems that are based on erosion or strictly heterogeneous chemical reactions, the release will involve the outward diffusion of the active agent or the inward diffusion of an aqueous environmental solution.

1. *Reservoir systems with a rate-controlling membrane.*

Microencapsulation produces a thin polymeric coating around solid particles, drops of liquids or dispersions of solids in liquids, with the size of the resulting capsules ranging from less than 1 µm to several thousand (Bakan, 1975). The methods of microencapsulation can be based on phase separation or coacervation, but interfacial reactions in emulsions or dispersions are more practical for agricultural applications. The wall comprises 5-30% of the formulation and the release rate can be varied by adjusting the microcapsule particle size, wall thickness and permeability (Scher, 1977). The rate of diffusion through the wall membrane depends on the concentration gradient across the membrane, the surface area and the thickness of the wall (Fick's Laws). Thus, a constant release rate is possible until the reservoir starts to become exhausted. In practice, this rate is not usually observed and rates decreasing with time are common.

Another reservoir system is the laminate, in which 2 or 3 polymer films are adhered or laminated together. The centre layer contains the reservoir, and diffusion through the barrier layer is regulated by the same principles as before (Kydonieus, Smith and Beroza, 1976). This formulation type can be prepared in sheet form and may be reduced to small "confetti" pieces. Due to size limitations, this is not sprayable, but is suitable for vapour release. Other membrane controlled types similar to the laminate are now available.

2. *Reservoir systems without a membrane.*

This group includes hollow fibres, impregnation in porous plastics, foams and fibres (Ashare, Brooks and Swenson, 1975). Hollow fibres are useful for the release of volatiles (Brooks, 1980) such as insect pheromones. The rate of release is controlled by diffusion through the vapour layer above the liquid surface. As evaporation continues the diffusion path increases and the amount released varies with the square root of time.

3. *Matrix systems.*

The active agent may be dissolved or dispersed in an inert polymer to give a matrix or monolithic structure. Polymers or elastomers compatible with the active agent are used and these types of formulations are simple and relatively inexpensive to prepare. Release occurs initially from the exposed surface and, in response to the concentration gradient set up within the matrix, more of the active agent diffuses out from the interior. Generally, the rate of release reduces with the square root of time (Baker and Lonsdale, 1974). As a result of the flexibility and economy of the matrix approach, a wide range of applications has been developed. The matrix becomes erodible if the polymer used is water-soluble or degrades during its intended life. Erodible and biodegradable formulations can break down completely, leaving no residues and are thus most suitable for tropical soil applications (Wilkins, 1978).

4. *Chemical bonded systems.*

The active agent may be protected from degradation in the environment by chemical bonding to a macromolecular substrate. The resulting polymeric derivative is naturally biologically inactive but the active agent can be released by breaking of the specific linkage which attaches it to the substrate polymer (Allan *et al.*, 1971). This approach is limited to those active agents which have at least one appropriate functional group. Also, the polymer must be suitably reactive. Release can be by abiotic hydrolysis, but the faster rate would be by microbial action. This mechanism provides an "environmental feedback", as release occurs when biological, and most pest, activity is greatest. In general, the rate of release depends on the type of substrate polymer, the degree of substitution, the nature of the chemical bond and environmental conditions. Release usually follows first-order kinetics. This approach to formulation is useful as many agricultural wastes and residues can be used as substrates or formulating materials (Jagtap *et al.*, 1983).

Applications in Tropical Agriculture

Of all the possible applications of CR (except the rapidly developing area in pharmaceuticals) those in tropical agriculture may hold the greatest potential. As a result of higher temperatures and other environmental factors the benefits of CR should be more distinct and allow the use of more desirable pesticides, without losing the obvious effectiveness of these substances. Thus, adoption of this approach is more urgent for tropical agriculture (and other related fields) than for corresponding temperate situations.

As in the cooler parts of the world, environmental conditions vary from time to time and with precise location. The lack of constant and reliable delivery pathways will reduce the maximum benefits theoretically possible. In practice, this could mean that small differences between CR formulations may disappear and that some of the simpler (and cheaper) types may perform as efficiently as the more sophisticated.

To conclude this presentation, some areas of potential in the tropics will be considered, and where field studies have been documented, these will be included. Preferably, such work should be continued over many seasons to confirm the performance under differing agricultural conditions, but this is difficult without a commercial interest. In this event, the information is usually less accessible.

Sprayable Systems

Due to the compatibility of microencapsulated formulations with conventional hydraulic spraying, this has to date proven to be the most popular approach for agricultural applications of CR. Commercial products range from insecticides (e.g., Penncap M, methyl parathion), insect pheromones for mating disruption of the cotton bollworm (Pectimone), herbicides (Capsolane, eptam plus antidote) to plant growth regulators (Cap-Cyc, chlormequat) (Wilkins, 1983). Although spraying equipment is less common in the tropics, the larger farming enterprises are equipped and this is likely to be the area where CR will be taken up initially. They will also be able to absorb the extra costs associated with specialized formulations.

Where warm and dry air conditions permit, the use of special formulations that form the microcapsules during spraying, "in-flight" encapsulation, could be appropriate for the tropics. Microcapsules, with sticking agents, are suitable for foliar applications as well as to the soil. The benefits sought will be extended persistence (of the order of weeks) for short-lived pesticides, better crop variety tolerance, safety to field workers and the exploitation of insect behaviour-modifying chemicals, such as pheromones, antifeedants or repellents (Campion, 1983).

Other sprayable methods include film or continuous polymer systems. Experiments with a special latex designed to form a film on foliar or soil surfaces have shown physical persistence on young coconut palms in the Philippines up to 3 months, without plant damage (author, unpublished work). The latex is formed from a polymer blend with a variable solubility parameter, a polymeric co-releaser and the active agent, designed to provide extended release. Emulsified polybutenes can be used to extend the effective persistence of pyrethroid insecticides, a valuable group for tropical use. Resins have already been shown to be useful in fungicide use in the tropics in this way (Couprie, 1977).

Controlled Release Granules

The use of conventional granules for herbicides and insecticides is popular in the tropics as these formulations can be applied by hand, with no need for equipment, which needs constant maintenance. Granules provide an excellent vehicle for CR, particularly the matrix types, which may be cheap to manufacture. Potential applications amongst soil applied pesticides include pre-emergent herbicides, soil and systemic insecticides, nematicides and fungicides. Further increases in targetting efficiency can be achieved by incorporation into seed dressings or by precision application methods, as used in European farming. However, granules fit in with both simple and advanced farming methods.

There are few CR granules commercially available at present. Most notable is a thermoplastic extruded granule containing 14% chlorpyriphos for use in plant sugarcane against cane grubs (McGuffog, Plowman and Anderson, 1984). This formulation will release for at least three years and protect the roots from attack over many cropping seasons. This type of CR allows the replacement of organochlorines (used widely in the tropics for soil insect control) by a short-lived organophosphate.

Release from biodegradable granules, based on forestry byproducts, especially kraft lignin, has been studied in detail by the author. This polymer, occurring extensively in plants, has an amorphous aromatic structure, and hence is an excellent protectant. It can form a matrix with many active agents and releases mainly through diffusion. Granules based on lignin, containing carbofuran, have been field trialled in tropical flooded rice with the collaboration of the International Rice Research Institute (Philippines), of MARDI (Malaysia) and SURIF (Indonesia), and supported by the Tropical Development and Research Institute (U.K.) over about 5 years. Depending on the situation, field trials have shown increased grain yields compared to the same dosages of conventional formulations, which supports the concept of increased efficiency of CR (Wilkins *et al.*, 1984). Brief details are in the Table.

Particle size and geometry are important and larger "granules" can provide extended protection for more permanent crops such as plantation and forest trees. For example, thermoplastic formulations of short-lived systemic insecticides placed

Field evaluation of carbofuran formulations root zone applied in rice (IR22) at transplanting, dry season 1981.

Formulation	Rate kg ai/ha	Productive tillers/hill (91 days after transplanting)	Virus %	Grain yield t/ha
CLF 45 (CR)	1.5	21.3 b	1.09 c	5.99 a
CLF 45 (CR)	0.5	20.5 bc	1.10 c	5.50 a
Furadan (conventional)	1.5	20.2 bc	0.62 c	5.75 a
Furadan (conventional)	0.5	17.2 c	23.00 b	3.56 b
control	0	18.4 bc	65.82 a	2.21 c

In a column, means followed by a common letter are not significantly different at the 5% level by DMRT.

in the planting holes of mahogany seedlings, in Costa Rica, have given protection for up to 2 years against shoot-boring lepidoptera (Allan, Gara and Wilkins, 1974). In tropical horticultural situations single plant treatment with membrane-enclosed CR formulations has increased the performance of pesticides and fertilizers dramatically (Peregrine *et al.*, 1981).

Controlled Release Baits

Baits can be very efficient in some pest control situations and improved release kinetics of the attractant can optimize this approach and also allow more ecologically subtle methods. An example could be similar to the use of the insecticide methoprene, against ant colonies, with the use of a bait. CR forms of growth regulators, fungicides or antibiotics could be used in baits against pests such as termites, which are not very amenable to biological control.

Ideally, the active agent would be released within the pest body or in the nest area. Resistance is unlikely with activity directed against the worker/soldier castes.

Microbial Pesticides

Many microbial pesticides (used mainly against insects, nematodes or weed plants) have persistence and availability problems similar to labile chemicals. Humid conditions are needed for activity, and protection from tropical sunlight is important. Thus, protection and release under optimum biological conditions are a requirement for all pesticides. Some success has been achieved in encapsulation of spores, particularly with mycoherbicides.

Controlled Release and Livestock

Protection of livestock under tropical conditions can be much more effective with CR technology. The frequent treatment of grazing animals is costly, often difficult and not always efficacious (e.g., in dipping, the bath is often depleted but use continues). CR technology has already demonstrated dramatic improvements against irritating flies and hornworms through plastic eartags. Season-long control can be obtained from a single treatment. However, the very efficiency of the technique has led to resistance in certain areas. This has given suspicion that the end of the release profile, when sub-lethal concentrations of the insecticide were present, augmented the emergence of resistance (Miller, 1985). This observation stresses the importance of the correct release characteristics in any formulation, and currently improvements are being made in these eartags. Although CR has been seen as detrimental for resistance management, this need not be the case, and CR can be used to overcome resistant insects. For example, microencapsulated diazinon can control resistant cockroaches because of the targetting efficiency of a single capsule.

Other delivery methods can be used on livestock. With ruminants, a CR bolus can be used to deliver trace minerals, growth stimulants, anthelmintics and agents against dung-breeding ectoparasites, as well as systemics (Laby *et al.*, 1984). Implantation (often in the ear) of a degradable polymer CR formulation can give protection for extended periods. These pharmaceutical techniques rely on the stable internal environment of the animal and avoid the random variation of the open.

Reduction in Hazards

Of particular importance in the tropics is the safe handling and application of the more toxic insecticides (plus one or two herbicides). This is largely a matter of training and education but an advantage of CR is that these hazards can be reduced. Accidental or intentional ingestion is less likely with granules and even liquid CR concentrates would have lowered oral toxicities compared with conventional formulations. In addition, such formulations are also less likely to be used for non-recommended uses. Paper and plastic sacks can be used for packaging, thus reducing costs and the potential re-use of the containers, as is the case for metal drums.

Manufacture of Controlled Release Formulations

In general, CR is based on the use of polymers, although other materials such as clays or certain inorganic glasses (which can also be considered as inorganic polymers) are used. Thus, local formulation in developing countries may depend on a polymer industry base. However, most tropical countries have an abundance of polymers as wastes or byproducts of agricultural and forestry or other processing, and these can be used in certain formulation types. The use of such raw materials for CR has been emphasized in the author's work, especially the use of lignocellulosics. Lignins are available from the pulp and paper industry and are normally burnt as process fuel or discarded. For formulation a portion could be diverted and isolated. Less processed wastes, such as bagasse, straw, rice husks, coir, etc. could also find a use in some types of CR formulations.

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