Atoms in agriculture: Nuclear techniques in "controlled-release" pesticide research

Under joint FAO/IAEA projects of the Seibersdorf Laboratories, research is forwarding the development of more efficient, safer, and environmentally less harmful pesticide formulations

by Manzoor Hussain

Traditionally, the problem of agricultural pest control has been dealt with by designing new, more potent pesticides. However, the use of pesticides often does not produce the desired biological response because of inabilities to deliver the pesticide to its target in optimum quantities and at the precise time.

When a pesticide is released into the environment, most of it is lost before it reaches its target. This loss occurs due to physical factors which move it away from the site of application and chemical breakdown. The physical losses occur due to evaporation, run-off from the surface of animal, plant, or soil, and binding with the soil or leaching. Chemical breakdown may result from photodegradation and hydrolysis or due to biological pathways in microorganisms. Thus, some pesticides are rapidly broken down while others are more persistent and may move from their placement site to cause possible detrimental side-effects and environmental contamination.

As a result of increased public awareness of the potential of persistent pesticides to cause harm to human health and the environment, there is greater emphasis on phasing out these compounds and on developing less persistent but more selective pesticides. The cost to develop a new pesticide has gone up and today may be US $20 million or more. This cost, in turn, is passed on to the consumer. Since less persistent pesticides require more frequent application, their use can be prohibitively expensive, especially for the developing countries.

Controlled-release pesticide formulations

Recognizing the cost and limitations in the design of new pesticides, the pesticide industry and scientists have turned to designing improved delivery of the pesticides, the newer and the older ones. An effective way to reduce environmental losses of pesticides is by using controlled-release (CR) technology. In the CR pesticide formulation, a pesticide and an excipient (usually a polymeric matrix) are combined to allow delivery of the pesticide to the target at controlled rates over a specific period of time.

The controlled release of pesticides from biodegradable substrates is not a topic new to nature. Many of the higher plants have evolved systems for controlling contiguous competitive vegetation by a phenomenon known as "allelopathy". For example, the absence of weeds around the cranberry plants after the flooding of cranberry bogs is attributed to herbicidal compounds produced in the leaves and delivered to the soil surface via leaching with water. The natural CR mechanisms provide non-active glucosides of the phytotoxicant. Therefore, further hydrolytic degradation must take place before the ordained herbicidal effect is observed. This exemplifies nature's way of utilizing biodegradable CR systems to maintain phytotoxic chemical concentrations.

The concept of controlled release of biologically active ingredients has been successfully developed over the last three decades by the pharmaceutical industry to provide safe and effective use of drugs and medicines.

CR technology offers the opportunity to improve efficacy of pesticides by protecting them against environmental losses. The amount lost to the environment is replaced by the amount released from the formulation until a balance is achieved. *(See accompanying graph.)* The objective is to deliver the pesticide to the target site at a constant effective level over a predetermined period of time. The formulation should be effective throughout the growing season of the crop but should not carry over to the next crop at unacceptable levels.

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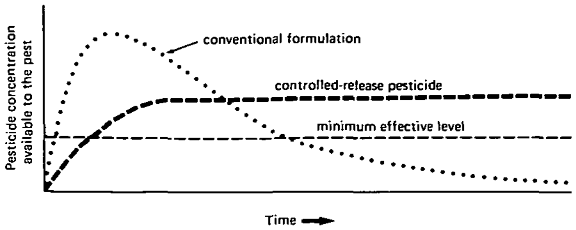
Conventional and controlled-release pesticide formulations



Shown are theoretical plots comparing when pesticide concentrations become available at a target site from conventional and controlled-release formulations.

In the case of a conventional formulation, the pesticide is released within a short time to provide a concentration greater than the optimum level needed. As it is lost to the environment, the effective amount is also depleted rapidly until it falls below the minimum effective level. In such a case, prolonged effective levels only can be achieved by repeated applications.

A pesticide can be physically entrapped within an inert matrix such as a polymer or can be chemically attached to it. The resulting system contains the pesticide which can be released by various means including diffusion, erosion, hydration, hydrolysis, biodegradation, mechanical rupture, and other means. The release rate depends upon the nature of the controlled-release system used, the mechanism of release involved, and physical-chemical properties of the pesticide involved.

Controlled-release pesticide formulations

Controlled-release (CR) formulations of pesticides can be divided into four main types:

Polymer membrane reservoir. These include microcapsules and microstrips.

- *Microcapsules* are sprayable and are generally in the 5–50 micron particle diameter range. They are composed of a liquid core of pesticide surrounded by a polymer wall (1).
- *Microstrip.* This is a sandwich-type system in which the active agent is contained in a central reservoir layer surrounded above and below by two protective layers (2).

Matrix containing physically-trapped pesticide. In this case, the pesticide is dispersed or dissolved in a polymeric matrix. The matrices may include rubber, polyvinylchloride (PVC), gypsum-wax mixture, polyester and acrylic resins, polyvinyl acetate (PVA), cellulose, starch, and gels such as alginate and lignin (3).

Covalently-bound pesticides. In this system, a pesticide is covalently-bound to a polymer which on cleavage (hydrolysis) releases the pesticide. Pesticide containing monomers also can be polymerized by additional polymerization (4).

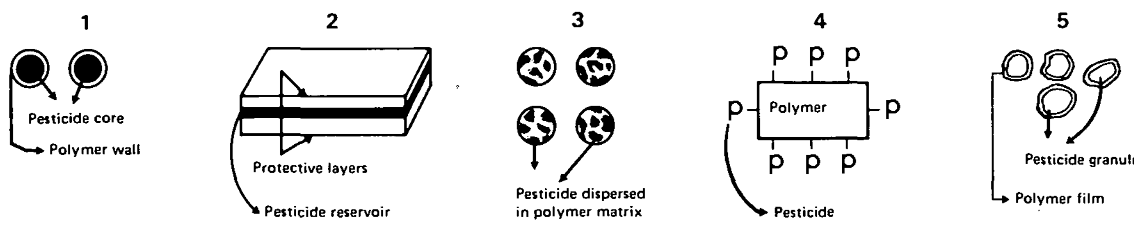
Coated pesticide granule systems. These consist of clay or other mineral granules of about 1 mm diameter impregnated with pesticide and coated with a polymer film. The polymer film controls the release of the pesticide (5).

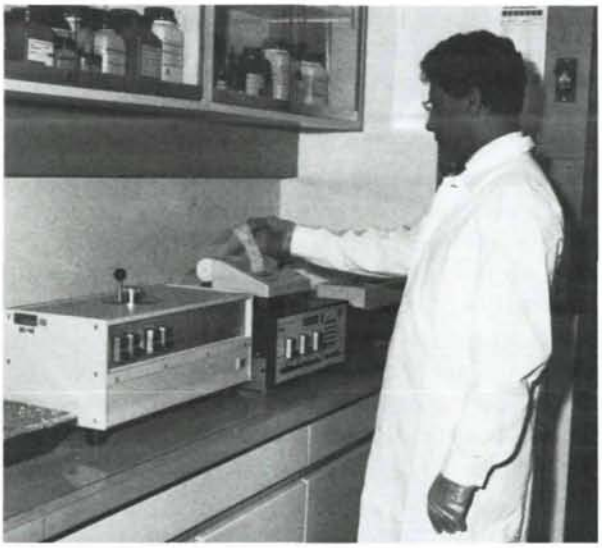
Advantages of controlled-release formulations include:

- Effective duration of non-persistent pesticides can be prolonged.
- The CR formulation allows much less pesticide to be used for the same period of activity resulting in less wastage and fewer applications.
- Losses due to environmental factors (evaporation, photolysis, leaching with water, degradation due to chemical and microbiological factors) are reduced. This results in savings in the cost of the active agent.
- Environmental contamination is reduced.
- Toxicity to non-target species of plants, mammals, birds, fish, and other organisms is reduced.
- Pesticides can be better targetted to desired areas and their efficacy can be improved.
- CR formulations are safer to applicators, handlers, and others coming in contact with the pesticides.

Disadvantages of controlled-release formulations include:

- Some CR formulations may require specialized application equipment.
- They may be more costly due to special development costs and more expensive inert ingredients.





A liquid scintillation counter is used for measuring pesticide-related radioactivity.

Radiotracers in pesticide research

The use of radiotracers in pesticide research is well established. This technique is one of the most accurate and reliable tools available to a pesticide chemist and is commonly used for quantitative and qualitative analysis of the pesticides and their degradation products.

The development of a CR formulation requires, as an initial step, a study of the rate of release of the active agent into the intended environment (e.g. air, water, and/or soil). This information is necessary and is used to manipulate the formulation to modify its release characteristics. The pesticide should be released at an optimum rate to be most effective. The amount of pesticide released into various components of the environment (soil, water, plants, fish, etc.) can be determined by periodic analysis of representative environmental samples. The samples can be analysed using conventional analytical techniques or radioanalytical techniques. The radioanalytical techniques are more sensitive and faster because there is less need for sample processing.

In a complex agro-ecosystem where a target pest has to be controlled without harming the non-target organisms, the rate of release of the pesticide from the formulation can be a decisive factor. For example, to control weeds in a rice/fish agro-ecosystem, it would be desirable to control the weeds without harming the fish. Many herbicides, when applied as conventional formulations at doses high enough to control weeds, are also toxic to fish. However, with a CR formulation, the herbicide would be released in quantities sufficient to kill the intended weeds but not harm the fish or other non-target species. It requires skillful manipulation of the formulation to achieve the desired rate of release of the pesticides. By using a pesticide tagged with a radioactive isotope such as tritium, carbon-14, phosphorus-32, or chlorine-35, the release of the pesticide from the formulation into the intended environment, such as water, can be accurately measured. The concentration of the released pesticide-related radioactivity is measured in a liquid scintillation counter.

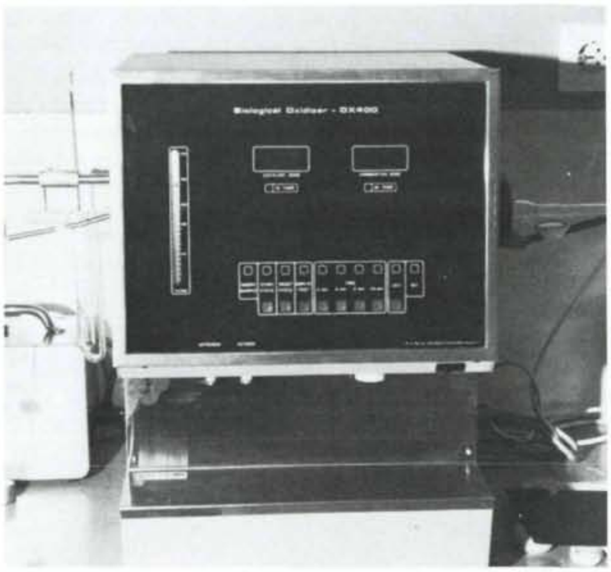
Conventional analytical chemistry techniques, such as chromatography, also can be used for these analyses. However, often the samples to be analysed require "clean up" prior to analysis by chromatography. Pesticide residues left unreleased in the formulation can similarly be determined more quickly by combustion of the formulation in an atmosphere of oxygen to carbon-14 dioxide which can be quantitated. On the contrary, it is not always possible to completely extract residues of non-radiolabelled pesticide from the formulation for analysis by conventional analytical methods. In most analyses, both conventional chromatographic as well as radioanalytical techniques are employed to supplement each other.

In addition to the determination of the release rate, other studies required for development of acceptable CR pesticide formulations include:

- the stability of the CR formulation under the expected environmental conditions and in storage;
- the fate of the released pesticide in soil, water, and other components of the environment;
- the uptake of the released pesticide by and distribution in the living organisms and the change in the levels of residues as a result of altered release rate.

The use of nuclear techniques can facilitate all these studies.

Residues of radiolabelled pesticides in CR formulations can be determined by combustion of the formulation in an atmosphere of oxygen to carbon-14 dioxide which can be quantitated.



FAO/IAEA supported research

The Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture since 1983 has sponsored internationally co-ordinated research programmes on the development of controlled-release pesticides. Research institutes from China, Hungary, India, Indonesia, Malaysia, Pakistan, the Philippines, Thailand, Tanzania, Belgium, the Federal Republic of Germany, the UK, and the USA have participated in these projects.

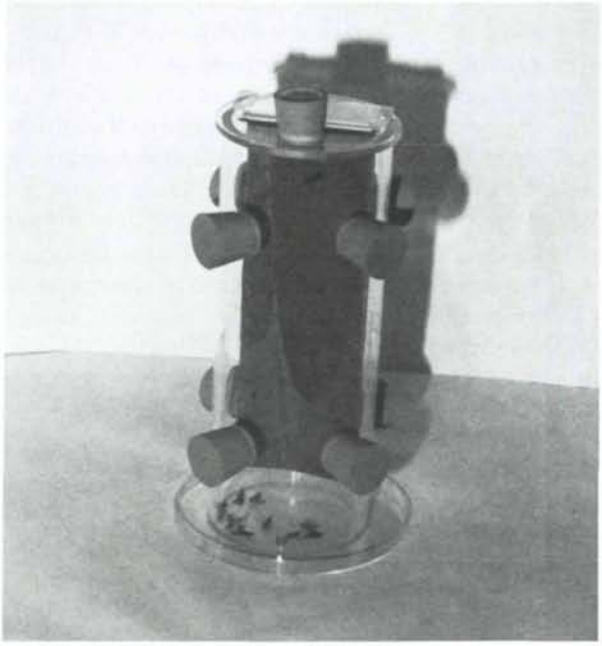
CR formulations of pesticides for various agroecosystems were prepared and tested. These included alginate formulations of DDT, dieldrin, and endosulfan insecticides; CR formulations of carbofuran insecticide in several biodegradable matrices including natrosol, latex, alginate, and kraft lignin; and CR formulations of pyrethroid insecticides deltamethrin, alfacypermethrin, and cyfluthrin. Similarly, CR formulations of several herbicides have been prepared and tested for weed control. These include alginate, natrosol, or latex-based formulations of butachlor 2,4-D, dichlobenil, terbutryne, and thiobencarb herbicides.

The results obtained from these research efforts clearly indicated that the development of potentially useful CR formulations of some of the tested pesticides was feasible and could result in the development of more efficient, safer, and environmentally less harmful formulations of these pesticides commonly used in developed as well as in developing countries.

Currently, the agrochemicals section of the Joint FAO/IAEA Division has a co-ordinated research programme entitled "Development of controlled-release formulations of pesticides using nuclear techniques". This project was initiated in 1988 and has two components: one relates to the development of CR formulations of insecticides for the control of tsetse fly, and the second involves the development of CR formulations of herbicides for the control of weeds in rice paddies and rice/fish ecosystems. Research contracts have been awarded to eight institutes from the developing countries and research agreements to three institutes from the United Kingdom and the United States.

Tsetse fly control. Insecticide-impregnated target screens are used in parts of Africa to keep the fly population in check and out of the uninfested areas. However, since the target screens are exposed to the open environment, the insecticides used on the targets are lost due to photolysis, leaching with rain water, and other environmental effects. This requires retreatments, resulting in an increased cost. The objective of the agrochemical section's research is to develop CR formulations of selected insecticides which will prolong the environmental life of the insecticide-impregnated target screens. Protection of the insecticide from loss due to ultraviolet (UV) radiation of the sun is a major objective because the insecticides found to be most effective against tsetse fly are also known to be sensitive to UV radiation.

Research is being done to develop controlled-release insecticide formulations for use in controlling the tsetse fly. Shown here is a tsetse fly target screen impregnated with radiolabelled insecticide being irradiated under an Osram ultraviolet sunlamp, and a bioassay of insecticide impregnated screen.



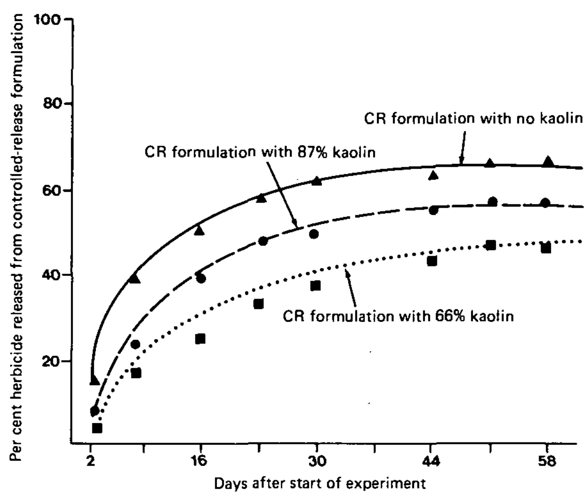
By using carbon-14-labelled insecticides and nuclear techniques, it was possible to show that some of the chemical compounds which absorb UV radiation, when added to the insecticide formulations, protect them from loss due to photolysis.

Other experiments have shown that leaching of the insecticides from the screens with rain water could be reduced by adding oils to the formulations. It is also desirable to attract the fly to the treated targets. Chemicals which have been reported to attract tsetse flies will also be included in the CR formulations. It is hoped that the combined efforts of the scientists co-operating in this project will result in insecticide formulations which will prolong the activity of the insecticides on the targets and will contribute to economical, efficient, and environmentally acceptable control of the tsetse fly in Africa.

Weed control in rice/fish ecosystems. Research on the development of CR formulations of herbicides for weed control in rice paddies and rice/fish ecosystems is proceeding in co-ordination with research institutes of China, India, the Philippines, Indonesia, Hungary, and Malaysia. Initial research at the IAEA's Seibersdorf Laboratories has indicated that formulation of thiobencarb herbicide in alginate matrix containing kaolin as a filler material can be prepared. The rate of release of herbicide labelled with carbon-14 from different formulations containing varying proportions of alginate and kaolin is under study. *(See accompanying graph.)*

Data collected so far indicate that the rate of release of the herbicide from the formulation can be altered by changing proportions of alginate and kaolin. These formulations are currently being tested in the greenhouse at the Seibersdorf Laboratories and by the co-operating institutes of several developing countries for their relative effect on the germination and growth of rice and species of weeds of economic importance. Studies on the relative safety of CR formulations of herbicides to fish will also be conducted at Seibersdorf as well as by the participants of the co-ordinated research programme. An ideal CR formulation of a herbicide will control the target weeds in rice or a rice/fish ecosystem without harming the rice plants, fish, or other non-target organisms and without leaving unacceptable levels of residues of the herbicide or its metabolites.

The rapid emergence of CR as an established scientific field is evidenced by the growing number of related publications appearing in the literature and the increasing number of symposia on the subject each year. Because of the rapidly increasing number of scientists working in this area, the Controlled-Release Society was established in 1978; in 1984, it started issuing the *Journal of Controlled-Release*. It is now a well recognized fact that CR technology can contribute positively to food and agricultural problems.



As part of the FAO/IAEA supported research of weed control in rice/fish ecosystems, radiotracers are being used to study different formulations of controlled-release (CR) herbicides. The graph shows data on the release of thiobencarb herbicide labelled with carbon-14 from CR formulations containing 1% alginate and different levels of kaolin.