IAEA-TECDOC-404

# RESEARCH AND DEVELOPMENT OF CONTROLLED RELEASE TECHNOLOGY FOR AGROCHEMICALS USING ISOTOPES

REPORT OF A SEMINAR
ON RESEARCH AND DEVELOPMENT
OF CONTROLLED RELEASE TECHNOLOGY
FOR AGROCHEMICALS USING ISOTOPES
JOINTLY ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND THE
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
HELD IN VIENNA, 1–5 JULY 1985

A TECHNICAL DOCUMENT ISSUED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1987

SITING OF RESEARCH REACTORS
IAEA, VIENNA, 1987
IAEA-TECDOC-403

Printed by the IAEA in Austria
January 1987

RESEARCH AND DEVELOPMENT OF CONTROLLED RELEASE TECHNOLOGY
FOR AGROCHEMICALS USING ISOTOPES
IAEA, VIENNA, 1987
IAEA-TECDOC-404

Printed by the IAEA in Austria
January 1986

The IAEA does not normally maintain stocks of reports in this series. However, microfiche copies of these reports can be obtained from

INIS Clearinghouse
International Atomic Energy Agency
Wagramerstrasse 5
P.O. Box 100
A-1400 Vienna, Austria

Orders should be accompanied by prepayment of Austrian Schillings 100,— in the form of a cheque or in the form of IAEA microfiche service coupons which may be ordered separately from the INIS Clearinghouse.

# FOREWORD

Pesticides are an essential element in agricultural production, and there is little doubt that their use will continue to increase as more food is demanded.

Pesticide usage may lead to the appearance of potentially undesirable residues as trace contaminants of food, the environment and living organisms. The full impact cannot, however, be quantified.

In recent years, increasing investment has been made into development of measures to reduce pesticide contamination of food and the environment while at the same time protecting crops and livestock from pest attack. In this context, the rapidly expanding controlled-release technology offers potential promise. Studies to develop controlled-release formulations are frequently carried out with isotope-labelled chemicals because of the precision with which they can be traced. Radiotracer techniques provide a unique tool in measuring the release rate of the chemical, the stability of the chemical within the formulation and evaluating the effect of environmental factors on the release rate.

These technologies and pesticide residue problems were the theme of the Seminar on Research and development of controlled-release technology for agrochemicals using isotopes, organized by the Food and Agriculture Organization of the United Nations and the International Atomic Energy Agency. It was held in Vienna, Austria, from 1 to 5 July 1985 and was attended by 54 participants from 29 countries.

The Seminar has illustrated the potential value of isotope techniques and has reviewed information on current developments in this field and their relevance to agriculture in developing countries.

# EDITORIAL NOTE

# CONTENTS

## 1. INTRODUCTION

### 1.1 Environmental losses of Agrochemicals

Chemical breakdown of an agricultural chemical occurs after it is released into the environment and, at the same time, the chemical is exposed to physical influences that can move it from the original site of placement. These two effects are responsible for losses of active material before it reaches its target. The amount of active ingredient that reaches the target organism after application represents the efficiency of the overall process. Losses that occur during application before the pesticide reaches the target and those that occur from the target itself (the target pest may itself provide the delivery pathway by moving towards the pesticide) depend on "weathering", i.e. physical dissipation of the material. Mechanisms by which this can occur include evaporation into the air and subsequent movement of material in air currents, suspension of material in liquid or solid dispersions which may then be blown away, wash-off by water from plant or other surfaces, leaching in the soil, and physical attrition. The probability that a particular active ingredient may be dissipated by one or more of these processes depends on its physical properties, e.g. vapor pressure, and on its lifetime in the environment or 'persistence'.

Persistence of a compound depends on breakdown either by non-biological pathways, such as hydrolysis or photodecomposition, or by biological degradation. The relative importance of these factors is determined by the chemical properties of the compound. Thus, some agrochemicals are rapidly broken down whilst others are much more persistent and consequently may move from their placement site to cause possible detrimental side-effects. However, in contrast to short-lived compounds which can break down more readily, these more persistent compounds undergo little degradation en route to the target and are more efficient in performing their biological function. This is In general, losses of pesticides in the environment follow a logarithmic relationship; the amount lost in unit time depends on the amount present. This gives rise to the concept of half-life; the time for the initial concentration to fall to one half of the original value.

In veterinary use, when drugs are administered to the domestic animals, loss by physical pathways is less important, while physiological elimination and enzymatic breakdown are the main loss of mechanisms. However, the efficient circulatory system generally provides a good delivery mechanism.

### 1.2 Benefits of Controlled Release

Controlled release has many potential benefits but the approach to increasing the efficiency of the use of biologically active substances, i.e. agrochemicals, is theoretically the most important consideration. To understand this we need to consider the rate of loss of an agrochemical, which we may assume follows first order kinetics. For example, an applied dosage of an agrochemical of 1 kg/ha declines to 500g in 15 days and to 250g in one month. This compound would then have a half-life of 15 days. The applied dosage acts as a reservoir to maintain the ambient concentration above a certain minimal level for activity. Assuming this rate of loss for the agrochemical, then the application of a level just above the minimum necessary for pest control (say 1mg) would provide protection for only a day or so. To achieve practical protection for periods of 50, 100 or 150 days, the levels of application would have to be increased 10-, 100-, or 1000-fold, respectively. In contrast, the theoretical level required to achieve these periods of protection is only that amount needed to maintain the minimum effective level of 1mg. Ideally, then, the pesticide should be continuously provided from an efficient reservoir at a rate exactly equivalent to the rate of loss that occurs after the initial treatment. If a pesticide were applied using just such an efficient reservoir, then the amounts needed to provide 50, 100, and 150 days of protection would be only about 3, 5, and 8 mg respectively. Thus there is a possibility of considerable saving in the amount of agrochemical used; the amount that is wasted increases logarithmically. This is of greatest importance with active agents of short half-life, e.g. insect sex pheromones, or in those cases where long periods of control are required.

Other benefits arise from this optimization of agrochemical use. Better targetting and reduced losses mean economic savings in the cost of the active agent. There is also reduced environmental contamination with less impact on non-target organisms, especially pest-controlling natural enemies and other beneficial organisms.

An equally important benefit lies in the safety of the new formulations, both for the pesticide applicator and for all those who handle and transport pesticides or subsequently come into contact with the "empty" containers .

In general, controlled release formulations can be used to reduce mammalian toxicity and extend activity; reduce evaporative losses; reduce phytotoxicity; protect active agents from environmental degradation; reduce leaching; and reduce pesticide levels in the environment.

### 1.3 Delivery Routes and Targets

The use of controlled release formulations implies the existence of appropriate delivery routes for the active agent from the macromolecular device to the target. In fact, to continuously replace lost pesticide as needed a controlled delivery system is required. Much will depend on the efficiency of this delivery pathway and neglect of this when controlled release systems are designed will lead to failure.

Examples of delivery routes include: blood circulation within stock animals from an implanted controlled release source; diffusion or mass flow in air or water for aquatic biocide or pheromone release; movement through soil followed by uptake and transport in plants for systemic pesticides; and continuous release to a surface where protection against later arriving pests is needed. Sometimes delivery routes or mechanisms can operate which are not used in conventional agrochemical applications.

The concept of delivery routes and release into different types of environment is important, particularly where the release is dependent on barrier effects. For the purpose of this report the formulations described have been categorized according to their application rather than the formulation type.

## 2. TYPES OF CONTROLLED RELEASE FORMULATIONS (H.B. SCHER)

Controlled release formulations can be divided into four main types: 1. polymer membrane-reservoir; 2. matrix containing physically trapped agrochemical; 3. covalently bound agrochemical, and 4. coated granule types. The polymer membrane-reservoir systems are diffusion controlled and include microcapsules and macrostrips. The matrix systems can be subdivided into inert and erodible categories. The release of agrochemical from an inert matrix is diffusion controlled while the release from an erodible matrix is controlled by the rate of degradation of the matrix. The rate of release of a covalently bound agent depends on the rate of cleavage of the specific chemical link attaching it to the polymer substrate.

### 2.1 Microcapsule systems

Microcapsules for spraying are generally in the 5–50/u particle diameter range. They are composed of a liquid core surrounded by a wall, usually polymeric and which constitutes of 5–20 percent of the microcapsule by weight. The processes used to microencapsulate agrochemicals are described later.

Examples of commercial microencapsulated pesticides include methyl parathion (Penncap M). The microcapsule wall is a cross linked nylon-type polymer produced by the interfacial polymerization of sebacoyl chloride/polymethylene polyphenyl isocyanate (dissolved in the pesticide phase) with ethylene diamine and ethylene triamine (in the aqueous phase).

In order to convert an aqueous dispersion of pesticide microcapsules into a finished formulation, the following ingredients must be added:

a. suspending agents to prevent the microcapsules from sedimenting
b. buffering agents to hold the pH of the formulation in the range which minimizes decomposition.
c. biocides to prevent biological attack of the water soluble polymers used in the formulation.

### 2.2 Macrostrip system

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. The Hercon$^{(R)}$ dispenser is the best example of this type and can be fashioned in large strips for household use or for field monitoring or can be chopped to a smaller size ("flakes") for application by dispersal. This dispenser is a reservoir with a diffusion controlling membrane and is therefore capable of release at a steady rate (constant or zero-order) The factors which affect the rate of release from this type of dispenser are.

a. reservoir concentration
b. membrane thickness
c. chemical functionality of the diffusant (active agent) compared to that of the membrane polymer
d. molecular weight of the diffusant
e. stiffness of the polymer (flexible vs. rigid PVC)
f. presence of co-diffusants, i.e. that are capable of altering the stiffness of the polymer

## 2.3 Matrix systems containing physically trapped agrochemicals

### 2.3.1 Inert matrix

In this case the agrochemical is dispersed or dissolved in a polymeric matrix that is not degraded by the environment. The rate controlling step in release from this type of formulation is usually diffusion in the polymer and the concentration is a function of time. This function is not constant but decreases normally with the square root of time. In this group are the rubber formulations for aquatic application; public health vector (insects and snails) control and weeds. Other matrices include polyvinylchloride with plasticizer such as the Shell NoPest Strip$^{(R)}$ containing DDVP insecticide for control of flies in a room or fleas on an animal, a gypsum-wax mixture, polyamide such as Altosid SR-10$^{R}$, containing methoprene, a juvenile hormone analog for adult insect control.

### 2.3.2 Film formers

Polymer film forming adjuvants can be added to pesticide formulations in organic solvents Ultra Low Volume (ULV formulations) or to aqueous dispersions to increase residual activity.

Polyester and acrylic resins dissolved in technical DDVP at the 33% and 17% levels and cellulose ether and polyvinyl ether maleic anhydride resins dissolved in technical mevinphos at the 1% and 2% levels extended residual activity significantly when applied as ULV applications without water. This method has been extended to achieve the "in-flight" encapsulation during spraying.

Water dispersible polymer latex adjuvants (polvinyl acetate) have been used to improve the adhesion of pesticides on foliage during prolonged rainfall and to reduce the toxicity of pesticides used in seed dressings.

### 2.3.3 Cellulose triacetate matrix

Sustrelle$^{(R)}$ cellulose triacetate microbeads (50/u) have a very porous internal structure and can hold up to 90% of other substances. These beads are suspended in water and control the release by diffusion.

### 2.3.4 Degradable or erodible matrices

Degradable matrices can contain dispersed or dissolved agrochemical. The matrix itself can be water soluble, degradable by hydrolysis unstable or biodegradable. The active agent can be released by diffusion from the polymer, by erosion of the polymer or by a combination of both diffusion and erosion.

This group of formulations includes:

a. mechanically formed (compaction, extrusion, agglomeration) granules using a mineral base and a binder.

b. gel (alginate, crossed-linked lignin) matrix

c. cross-linked starch (xanthide, borate) and PVA polylactic acid matrix.

### 2.4 Polymer systems containing covalently bound agrochemicals

The rate of release of an agrochemical covalently bound to a polymer depends on the rate of cleavage (hydrolysis) of the specific linkage which binds it to the substrate.

$$\text{polymer} + \text{pesticide} \underset{\text{hydrolysis in the environment}}{\overset{\text{synthesis}}{\rightleftharpoons}} \text{polymer-pesticide}$$

This method is limited by the functionality requirements of the pesticide and by the natural hydrolysis rate of the product. This latter is dependent on the hydrophilicity of the resulting combination and if this is too low then the polymer will be too stable in the environment for effective release and control. An additional problem with this type of formulation may be regulatory, if the national registration authorities, consider that such a formulation constitutes a novel (thus untested) compound. A large number of such polymers have been produced and tested. They have been based on preformed synthetic (PVA) or natural (cellulose, starch, lignin, protein, chitin, keratin) polymers. Other approaches include the formation of pesticidal derivatives and polymerization of pesticide-containing monomers, particularly by addition polymerization. Many are successful in field tests. One such tin-containing polymer is used as a long-life anti-fouling paint for ship bottoms.

### 2.5 Coated pesticide granule systems

These generally consist of clay or other mineral granules of about 1mm diameter, impregnated with agrochemical and subsequently coated with a polymer film.

#### 2.5.1 Granules coated with urea-formaldehyde resin

Urea-formaldehyde mixtures or urea-formaldehyde prepolymers are mixed with acid catalysts (phosphoric, sulfuric acid, etc.) which are then sprayed onto the granules. The mixture is rapidly agitated during the polymerization reaction. After 30 minutes of stirring a friable, substantially dry, readily handled product is obtained. In the soil these granules release the active agent by gradual decomposition of the polymer resin.

#### 2.5.2 Fluidized bed spray coating

In the Wurster fluidized bed spray coating process, a fluidized bed of pesticide granules is sprayed with an aqueous polymer solution or dispersion of active ingredient. Coating occurs when the water is evaporated. Additional coats of polymer can be applied to the granules by recirculation through the spraying and drying zones. Agglomeration of the granules is minimized by alternately spraying and drying. Aqueous coating systems used in this process can be grouped as follows:

a Water soluble polymers: hydroxypropyl cellulose, polyethyleneoxide, hydroxypropyl methyl cellulose.

b. Water dispersible colloids: gums, starches

c. Polymer lattices: polyvinylidene chloride, polystyrene, polybutadiene.

### 2.5.3 Agrochemical impregnated carbon granules

Activated carbon granules can strongly adsorb organic pesticides which can then be slowly desorbed (released) into the environment. No coating is necessary to achieve slow release.

## 3. SUMMARY OF MEETING

As pesticide use increases in the developing world, there has been considerable interest in controlled release systems for crop, animal and public health applications. Particular benefit could be derived in tropical situations, mainly in improved efficiency and better safety, and the use of isotopes in research and development would appropriate for enhancing the progress and promoting the uptake of this new, technology suitable for developing countries.

This Seminar has been intended as a forum for disseminating information on the current status of controlled release technology for agrochemicals, to bring attention to the applicability of isotope use in this research and to exchange points of view relevant to many parts of the developing world. This report on the Seminar is intended to further this process of information and education.

## 4. SEMINAR VENUE AND OPENING

The Seminar was held in the Vienna International Centre and at the IAEA Laboratory in Seibersdorf, Austria, from 1 to 5 July 1985. A total of 54 registered participants attended from 29 Member States and 4 International Organizations. There were 23 papers, including 8 invited speakers, from 14 countries and 2 organizations. A general Panel Discussion was included and the last two days were devoted to a practical workshop at the Seibersdorf Laboratory where aspects of preparing formulations were demonstrated and discussed (see Section 9).

The Seminar was opened by Professor M. Zifferero, Deputy Director General, Department of Research and Isotopes, International Atomic Energy Agency. Mr. J. Henriet, Member of the FAO Expert Group and Head of the Chemistry Laboratory of the Phytopharmaceutical Station of the Ministry of Agriculture in Gembloux, Belgium, gave an introductory speach on behalf of FAO.

## 5. SCIENTIFIC SESSIONS

The sessions were organized on the basis of the types of controlled release formulation technology currently available and on application areas. After an overview of the technology, the specific formulation types appropriate to agrochemical delivery were described. Scientific sessions then covered pesticide, pheromone, and veterinary applications and pest problems and the use of isotopes. The papers given in these sessions are reported in the subsequent chapters with emphasis on the educational and practical aspects, such interpretation being the responsibility of the editor. Those readers who wish to have further details should write to individual authors whose addresses are provided at the end of the report. The use of isotopes for studying release from formulations has, as yet, not been used extensively, partly because the cost of synthesizing labelled agrochemicals is often high and also because there may sometimes be difficulty in interpreting the measurements of the released agent. However, where the labelled agrochemical is available it more facile and extensive monitoring are possible under a wide range of environmental conditions.

## 6. PANEL DISCUSSIONS

A general Panel Discussion was held under the Chairmanship of Mr. J. Henriet. The panel members were:

S. Barzin, USA
K.G. Das, India
K.J. Ellis, Australia
J. Henriet, FAO
J.R. Plimmer, IAEA
B. Sugavanam, UNIDO

A wide ranging discussion followed. Areas of concern expressed by the participants included availabality of information and advice relevant to developing countries, technological matters and the possibilities of problems that may be associated with controlled release formulations of agrochemicals.

Information is needed on the relevance to developing countries of controlled release, particularly on the areas where this approach could be valuable. Education is needed on this new technology and guidance was sought regarding standardized testing procedures. In field testing, details such as experimental design, observations, replicates, etc. are required. It was felt that here the co-ordinated agency research programmes with a common focus were useful. The ability to compare results would be valuable. Assistance in providing links among workers in different countries is needed.

On technological matters, it was felt that complete exhaustion of the formulation was prerequisite and thus biodegradable materials were generally preferred. Of particular importance, are the use of controlled release formulations for stored product pest control which could involve microcapsules, alginates or packing materials that incorporate repellents. In such cases it is important to know what residue problems might be anticipated.

Potential problems that could be associated with the use of controlled release formulations include the prolongation of a sublethal period and the exacerbation of the problems of pesticide resistance especially with insects. It is desirable that formulations should have a definite period of release with a sharp termination. The apparent reluctance of some major US companies to use long-term pesticide release formulations was cited. Comments were made on the problem of increased rate of degradation of soil-applied pesticides in soils which had received repeated applications. This problem might become even greater, if controlled release formulations were used. A possible remedy may be the incorporation of bacterial inhibitors into the formulation. Concern was also expressed regarding the possible hazard of spent formulation material (especially to livestock). This emphasized the requirement for substantial breakdown of the polymer substrate.

## 7. CONCLUDING SESSION

During the concluding discussion, it was agreed that greater familiarity with controlled release technology was important to the developing countries. The benefits were clearly of importance and the effects of the tropical climate on agrochemicals were insufficiently understood compared to the extent of knowledge of their fate and behaviour under temperate conditions. Many of the participants were not aware of the technology prior to the Seminar. Greater exposure to the technology should be encouraged for developing countries and the Seminar had made a successful beginning. Promotion and dissemination of information is needed and a newsletter was proposed. In this respect, reaction from participants of the Seminar was invited.

Mr. J. Henriet thanked, on behalf of the participants, the sponsoring organizations and staff. Dr. J.R Plimmer thanked all participants, chairmen, and speakers for their interest and dedication and officially closed the Seminar.

## 8. TECHNICAL PRESENTATIONS

### 8.1 Microencapsulation

### 8.1.1 Microencapsulated pesticides (H.B. Scher)

As mentioned in the previous chapter (2.1) microcapsules are 1-200 micron particles composed of a solid or liquid core surrounded by a wall The wall is generally polymeric in nature and constitutes 5-25 percent of the microcapsule by weight. The wall isolates and protects the core material in storage but is designed to release the core contents in a controlled fashion when the microcapsules are exposed to the environment. The core material can be released by crushing the wall by pressure from within, dissolving the wall, hydrolyzing the wall or by diffusion through the wall

An aqueous dispersion of pesticide microcapsules is a particularly useful controlled release pesticide formulation because:

a. It is composed of discrete microcapsules as opposed to aggregates.

b. It can be diluted with water or liquid fertilizers and sprayed using conventional equipment. Uniform field coverage of pesticide is possible.

c. It requires less polymeric component per kilogram of pesticide than monolithic devices.

d. It is capable of establishing a constant pesticide release rate.

e. The pesticide release rate can be varied over wide limits by varying the microcapsule particle size distribution, the microcapsule wall thickness and the microcapsule wall permeability.

f. Additives such as film-forming agents can be added directly to the formulation. These agents can improve the adhesion of microcapsules to foliage.

There are three microencapsulation processes. In the phase separation category, the core is emulsified or dispersed in an immiscible continuous phase in which the wall material is dissolved. The wall material is then caused to physically separate from the continuous phase and deposit around the core particles. Examples are:

a. Aqueous phase separation (complex coacervation) - National Cash Register Company.

b. Organic phase separation - IBM

c. Meltable dispersion - NCR

d. Spray drying - Moore Business Forms, National Starch and Chemical Corporation

e. Fluidized bed coating - Smith, Kline and French, Wisconsin Alumni Research Foundation.

In the interfacial reaction category, microcapsules are formed by emulsifying or dispersing the core material in an immiscible continuous phase and then an interfacial polymerization reaction is caused to take place at the surface of the core particles. Methods used here are:

a. Interfacial condensation polymerization - Pennwalt
b. In situ interfacial polymerization - Stauffer Chemical Company
c. Interfacial addition polymerization - Stanford Research Institute, NCR

In the physical methods category, wall material and core particles are physically brought together and the wall flows around the core particle to form the microcapsule. This approach includes:

a. Multiorifice centrifugal - Southwest Research Institute
b. Electrostatic - III Research Institute.

Some common microcapsule wall materials are:

gelatin
sugar
carboxymethyl cellulose
polyethylene
polyacrylamide
polyamides
polyisoprene
epoxy resins

gum arabic
ethyl cellulose
polypropylene
polyethers
polyureas
polysiloxanes
inorganic silicates

starch
paraffin
polyvinyl alcohol
polystyrene
polyesters
polybutadiene
polyurethanes

Complex coacervation, interfacial polymerization and In Situ Interfacial polymerization are the most widely used processes for microencapsulation of pesticides. The resulting product of these processes is an aqueous dispersion.

For 20 years the National Cash Register Company has used an aqueous phase separation process (complex coacervation) to microcapsulate pesticides. The process consists of the following steps:

a. Dissolve gelatin (isoelectric point = 8) in aqueous phase (pH 8.0; $5^{o}$).

b. emulsify pesticide liquid in aqueous phase.

c. add gum arabic solution to the aqueous phase (pH 8.0; 5°).

d. mutual precipitation of gum arabic and gelatin around particles is induced by reducing pH to 4.5 and diluting with water.

e. gel complex coacervate by cooling to 5-1°C.

f. Harden complex coacervate by addition of glutaraldehyde or formaldehyde and adjusting pH to 9-10.

Organic phase separation and meltable dispersion processes are the inverse of aqueous phase separation and are used to microencapsulate hydrophilic substance. Organic phase soluble polymers are precipitated around the hydrophilic core by the addition of a nonsolvent or cooling. Since pesticides are often lipophilic these processes are less common.

Spray drying and fluidized bed spray coating are useful processes for pesticide encapsulation. In the spray drying process, a film, forming polymer is dissolved in the aqueous continuous phase of a pesticide dispersion. The drying process causes the water to evaporate and the polymer coats the pesticide particle. The resulting product is a free-flowing dry powder. In the Wurster process (fluidized bed spray coating), a fluidized bed of solid pesticide particles is sprayed with an aqueous polymer solution. Coating occurs when the water is evaporated. Additional coats of polymer can be applied to the particles by recirculation through the spraying and drying zones.

Pesticide microcapsule powders can also be produced by multiorifice centrifugation or electrostatic encapsulation. The diameters of the microcapsules produced are limited to 80u and larger.

### 8.1.2 Microencapsulation by interfacial polymerization

The *in situ* polymerisation process was used to produce microcapsules. The organic phase containing pesticide and the isocyanate monomers (polymethylene polyphenylisocyanate, PAPI and toluenediisocyanate, TDI) was dispersed into an aqueous phase containing an emulsifier and protective colloids The wall forming reaction was initiated by heating the batch to an elevated temperature, at which point the isocyanate monomers are hydrolysed at the interface to form amines which, in turn, react with unhydrolysed isocyanate monomers to form the microcapsule wall. This can produce formulations containing 4-5 pounds of active ingredient per gallon.

$-NCO + H_2O \rightarrow -NH.COOH \rightarrow -NH_2 + CO_2$

isocyanate carbamic acid amine carbon dioxide

$-NCO + -NH_2 \rightarrow -NH.CO.NH-$

isocyanate amine polyurea

The release rate of this microcapsule type can be varied by changing the following:

a. Microcapsule size (i.e. total surface area per unit quantity of pesticide).

b. Wall thickness (i.e. weight percent isocyanate monomers in organic phase).

c. Wall permeability - for methyl parathion release the rate can be increased by reducing the ratio of PAPI to TDI at fixed particle size and fixed wall thickness. The permeability can also be increased by the addition of ammonia during the course of the reaction. This reduces cross linking. Permeability can be reduced by formation of the wall in the presence of a good solvent, which reduces the size of micropores in the wall.

### 8.1.3 Microencapsulated thiocarbamate herbicides (H.B. Scher)

The thiocarbamate herbicides EPTC + protectant (Eradicane), butylate + protectant (Sutan), and vernolate + protectant (Surpass) are well established maize herbicides and can control many important grass weeds. Most thiocarbamates are volatile and must be incorporated into the soil immediately after application. This restricts their use in many countries. This drawback can be overcome with encapsulation using *in situ* interfacial polymerisation. Reduced mammalian toxicity, increased selectivity, reduced soil movement and the prospect of lower application rates are other benefits.

Typically the products are aqueous suspensions of 1-200um sized particles, at 360g/l for EPTC and 480g/l for vernolate, together with suspending and buffering agents.

A large number of field trials were conducted throughout Europe during 1979 and 1980 to evaluate these formulations. The main objective was to determine whether soil incorporation could be delayed for a period of 24 hours after application without loss of activity. The results of this testing confirmed that this was so under a wide range of soil and climatic conditions.

## 9. CROP AND PUBLIC HEALTH APPLICATIONS

### 9.1 Application to soils

### 9.1.1 Controlled release formulations of carbofuran and other pesticides (K.G. Das)

There is a need to develop a controlled release carbofuran formulation, particularly to control leaf and plant hoppers. Those from rice growing countries (Asia) can understand the importance of this for localized application as carbofuran is one of the most widely used insecticides in rice cultivation. Carbofuran has high mammalian oral toxicity. It is also known to degrade rapidly in soil. Root zone application has been demonstrated to be the most effective The current application of 3G granules offers protection to the plant for only about 21 days and the quantity of active agent which is effective is about 1/3 of the amount applied.

Under the FAO/IAEA/GSF research programme to develop and evaluate controlled release formulations of pesticides to reduce residues or increase efficacy utilizing isotopes, a controlled release carbofuran formulation was developed for soil application. Carbofuran is not suitable for chemical bonding to a polymer. Hence a physical approach was adopted. Coating is one of the physical methods of controlling release. Polyethylene was selected as the polymer matrix. Since commercial polyethylene is crystalline, it was found necessary to give a solvent treatment to make it suitable for use as a matrix. Using solvent treated polyethylene, kaolin and talc a controlled release formulation in the form of pellets was made.

The release rate of carbofuran from the pellets into water were determined using $^{14}C$-labelled carbofuran. The radioassay was carried out every week for eight weeks. About 80% of the carbofuran was released nearly uniformly in eight weeks.

A root dip formulation was prepared containing 3% carbofuran, using bentonite, GM powder, carboxymethyl cellulose and glue.

A controlled release abate formulation to control mosquito larvae was developed in the form of floating pellets. Solvent treated polyethylene was used as the polymer matrix and talc was added as a filler. The rate of release of abate from the pellets into water was determined for a period of twenty weeks by both chemical and bioassay techniques. The rate of the release was uniform over this period. After twenty weeks the pellets sink.

In a chemical approach, a pesticide was covalently bonded to a polymer. A controlled release granule formulation of 2,4-D was prepared by converting it to the acid chloride and reacting this with dry sawdust. The requisite amount of free 2,4-D is added to provide a high initial dose. The efficacy of the formulation was determined by multilocational large scale field trials in rice, wheat, jowar, bajra, sugarcane and groundnut. The esterification was scaled up to pilot plant size and prepared in large batches over three consecutive years. The product is now waiting registration.

### 9.1.2 Biodegradable polymeric formulations of carbofuran, 2,4-D and other pesticide (R.M. Wilkins)

Biodegradable by-products from agricultural, forestry and related industries provide considerable quantities of low-cost polymers and they can be used as formulating agents for controlled release systems. Potentially useful waste- and by-products include sawdust, bark, cereal husks, straw, bagasse, coir, lignin (both from pulp and paper making and from biomass hydrolysis residues), starch, chitin (from crustacea), waste proteins (hair and hide), as well as partly processed derivatives as waste paper, and other industrial and domestic wastes. Pesticides and other biologically-active substances can be chemically or physically incorporated into these polymers to provide a range of formulation types.

Particularly valuable are the lignin residues as these can provide either chemically or physically modified structures. Alkali lignins, with a unique, randomized structure, aromatic in nature possesses many features which are both invaluable, both in its native state in the living plant and for protection of pesticides in solid formulations.

These are:

a. Ultraviolet protectant
b. antioxidant
c. inhibitor microbial activity
d. excludes water but is hydrophilic and can be plasticized/solvated
   by polar substances including many pesticides

The physical method is easier and more economic. In this situation, compatability of the lignin (alkali or kraft ) with the pesticide depends on the appropriate solubility parameters, in order to form a cohesive solid matrix.

The active agent and lignin may be incorporated to form the matrix by heating to about the melting point and mixing. Alternatively, a solvent may be used to achieve this mixture, after which solvent must be removed.

The matrix formed by this method is most heterogenous, releasing active ingredient by a process of diffusion and dissolution, leaving a porous, friable material which collapses completely, ensuring total exhaustion of the original pesticide content.

The carbofuran-lignin formulations were evaluated in tropical flooded rice over a period of 4-5 years, with the collaboration of the International Rice Research Institute (IRRI) and with the support of the Tropical Development and Research Institute of the British Overseas Development Administration. Assessment during this period included effects on insects (also laboratory-reared insects inserted into field caged rice plants), on growth of the crop and on diseases including the damaging rice tungro virus. Where the virus was endemic, grain yields were increased. In fact, the same yield was achieved with 0.5 kg carbofuran/ha. in lignin granules as with 1.5 kg carbofuran/ha. in the form of conventional clay-based granules.

2,4-D lignin studies. Earlier work had indicated the compatibility of 2,4-D with kraft lignin. When prepared in the form of a 50% CR formulation, the formulation showed value as a low cost aid in reforestation by coniferous trees. When seedlings (2-3 years old) are transplanted from the nursery, they suffer severe weed competition, especially in the first year following transplantation. This problem is greater under tropical conditions. A localized surface application of the lignin composition around the seedling at planting reduces weed growth for 1-2 seasons. Also observed was an auxin-like stimulation of the crop growth leading to greater growth and better establishment of the young trees.

### 9.1.3 Slow release, mobility and applicability of pesticide microcapsules

(Y. Mualem, A. Marcus, S. Friedman, C.S. Helling, N. Lahav, N. Aharonson)

The objectives of this study were to produce microcapsules, investigate their slow release characteristics, dispersion in water, mobility in soil and effectiveness in bioassays. Two herbicides, atrazine and trifluralin, were chosen as models, representing properties of different groups of pesticides. Two different techniques of microencapsulation were examined. polycondensation at the interface between two phases and phase separation. A wide variety of atrazine microcapsule types and also a few trifluralin microcapsules were produced. Wall materials were polyurea, polyurethane, polyamide and fatty acids. For each type the active ingredient content was determined by analysis. Size and shape of the microcapsules were determined using sedigraph and electron microscope techniques.

The use of dispersing agent improved the suspension stability of the microcapsules in water and reduced aggregation. Microcapsule mobility in porous media was investigated on a comparative basis by observing breakthrough curves (rate of movement of the microcapsules) using sand columns with lengths between 5.5 and 22 cm, and saturated with water. The mobility was high in clean sand but was reduced considerably for unaggregated sandy loam.

## 9.2 Application to Surfaces

### 9.2.1 Controlled release formulations of insecticide for improved efficacy against tsetse flies (L. Vollner, C. Pascucci, H. Perschke)

Endosulfan has a very short half-life of three to seven days. Thus high dose rates (250-1000 g/ha) are used on plant surfaces, and this may also cause damage to mammals, reptiles, birds, fish and other non-target organisms. To improve the performance of endosulfan (i.e. to reduce dose rates or frequency of application) a controlled release formulation based on alginate gel was prepared. This matrix allows not only uniform distribution of the pesticide but also protects it against rain, humidity, temperature and UV radiation.

Sodium alginate was selected as a formulating agent because of its low toxicity, biodegradability, broad chemical compatibility and ease of preparation.

To evaluate the alginate gel formulation of endosulfan, crosslinked with calcium the following tests were made:

a. leaching with water in a column
b. codistillation with water
c. stability to UV radiation
d. evaporation under dry conditions
e. biological activity against tsetse flies or mediterranean fruit flies
f. residual activity on maize plants

Although the volatilities of the two isomers of endosulfan are different (alpha being more volatile than beta), the alginate formulation extended the residual lifetimes of both isomers three- to four-fold, when compared with the conventional emulsifiable concentrate (e.c) formulation. In the simulated field experiment, residual amounts of endosulfan on plants treated with the alginate formulation were 2-3 times higher than those remaining after treatment with the e.c. formulation.

In conclusion the alginate gel formulation could considerably improve the efficacy of endosulfan in tropical regions. It delays release of the chemical and provides protection against tropical temperatures, rainfall and intense ultraviolet radiation. Environmental contamination would also be minimized because reduced amounts and less frequent applications are required.

## 9.3 Aquatic Applications

### 9.3.1 New copolymer with pendent organotin moieties as controlled release mosquito larvicide (A.M. Wakid, N.M. Hilmy, A.F. Shaaban)

A new copolymer formulation was prepared and assayed for its efficacy as a controlled release mosquito larvicide. It was prepared from the reaction of the bis-n-tributyltin oxide (TBTO) with itaconic acid to give the monomer tri-n-butyltin itaconate (TBTI). The copolymer of TBTI with methyl methacrylate (MMA) was obtained by solution polymerisation in the presence of azo-bis-isobutyronitrile as a free radical initiator. The resulting purified copolymer was colourless, transparent and suitable for film formation. Films were prepared from the purified TBTI-MMA copolymer solution (50% in toluene) on PVC or glass plates and left at room temperature to complete dryness.

For biological assay a stock colony of the mosquito. *Culex pipiens* was maintained in the laboratory for several generations. Dry PVC plates painted with the copolymer were hung in enamelled pans containing tap water and third instar mosquito larvae to study the toxic effects on them.

The results obtained showed that larval mortality was clearly affected and increased with time. Hundred percent mortality was reached after 10 weeks of continuous exposure to the formulation without changing the original water. However, in the case of weekly changes of water, the percent larval mortality showed fluctuations when plotted against time. Larvae younger than third instar were more susceptible to the formulations than older ones. Although egg rafts were able to hatch, all the resulting larvae died in the first or second instar. Pupation was delayed and the pupated larvae showed abnormal emergence or died before completing their life cycle. The released toxic compounds showed gradual degradation to non-toxic compounds with a half-life of less than four weeks. The formulation toxicity was affected by change in the pH of the larval medium. In neutral media (pH 7), the larval mortality was much lower than in acidic media (pH 5). The highest larval mortality was observed in alkaline media (pH 9).

### 9.3.2 Slow release formulation of terbutryn using natural rubber and irradiated latex (M. Sumatra, M. Utama)

Terbutryn is a selective herbicide for pre- and post emergence weed control. It is registered for post emergence weed control in winter wheat and barley and also on grain sorghum in the USA. It has been suggested that this herbicide could be formulated to control water hyacinth and hydrilla. It is moderately toxic to fish. The weeds grow rapidly in the aquatic environment and become a serious pest in many developing countries. Repeated application of conventional formulations of herbicides to lakes, dams or canals may cause environmental pollution and endanger man and other non-target organisms. Slow release formulations can minimize these undesirable effects.

Rubber based matrix formulations have been used to provide extended release of herbicides for aquatic weed control. Generally, sulphur and elevated temperatures are used to induce cross linking by vulcanization. This can also be effected by using Co-60 gamma rays.

In this study irradiated natural rubber latex was used to coat the herbicide formulation containing blended crumb rubber, terbutryn, carbon black and stearic acid.

The composition of a slow release formulation was as follows:

| | | |
|---|---|---|
| a. | crumb rubber | 100 g |
| b. | Igran 80 WP (terbutryn) | 40 g |
| c. | carbon black | 20 g |
| d. | stearic acid | 0.2 g |
| e. | irradiated latex as required to obtain a thin film. | |

The crumb rubber was impregnated with Igran 80WP and other ingredients using two different-speed rollers and blended until they were mixed thoroughly. The mixture was then prepared as a sheet of 2 mm thickness. It was cut in pieces 5 x 10 cm. Three different formulations were prepared as follows:

a. formulation 0 : no further treatment
b. formulation 1 : dipped once in irradiated latex and
c. formulation 2 : dipped twice in the irradiated latex with an interval of two hours in between two dips and then dried at room temperature. Each dipping resulted in a 0.01 mm film thickness.

Release studies were performed on samples of 1g each in 1 liter of Hoagland solution. Release of the herbicide was monitored by water analysis using high performance liquid chromatography (HPLC) or a bioassay using Salvinia natans, for a period of 18 weeks. Results indicated that extended release was obtained and that the latex coating did reduce the amount released. The experiments made in the presence of the weed showed that it strongly absorbed the herbicide after release.

### 9.3.3 Controlled release pesticides by formulation with thermoplastic polymers (G. Pfister, M. Bahadir, F. Korte)

For practical application in agriculture, horticulture and related fields the necessary production of controlled release formulation on a large scale depends on the availability of sufficient amounts of matrix materials and on methods for their production at moderate cost. Therefore, the use of common plastics, which are produced in high quantities and for which there are numerous proven process methods, seems to be advantageous for this purpose.

In our investigations, we used low density polyethylene (LDPE) and ethylene-vinyl acetate copolymers with varied content of vinyl acetate to prepare controlled release formulations of the monolithic or matrix type. Mixtures of the active agents with the powdered or granulated polymers can be processed by an extruder to endless cables, strands and sheets, according to the application required. With a selection of pesticides of different chemical classes and physico-chemical properties, conditions for homogeneous incorporation into polymers have been studied. Active ingredients were the insecticides propoxur, lindane, endosulfan, carbofuran, chlorpyrifos, parathion, chlorfenvinfos and DDVP, the herbicides monolinuron, metoxuron, desmetryn, terbutryn, atrazine, 2,4-D, chloridazon, diquat dibromide and dichlobenil

A basic condition for the preparation process described is the thermal stability of the active agent through a range of temperatures about 120-160°, which is maintained during extrusion. There was considerable thermal decomposition insecticide propoxur to isopropyl alcohol and, probably, methyl isocyanate, while considerable quantities of DDVP evaporated because of its relatively high vapour pressure. These two substances therefore could not be formulated by this method.

With DDVP and the other liquid organophosphates parathion and chlorfenvinfos, sufficiently homogenous mixtures with the polymer granules could not be obtained at first because most of the liquid phase separated after a while. The addition of 10% of polymer powder with its larger adsorbing surface helped to stabilize the mixtures, which could then be extruded without problems.

Substances with melting points above the extrusion temperatures and with low solubilities in the polymer melt, e.g., chloridazon and diquat dibromide, can be incorporated in the polymer matrix only as dispersed particles. In general, the solubilities of the active agents in the polymer mix increase with the increasing content of vinyl acetate and with decreasing polarity of the active ingredient.

The release of equal amounts of monolinuron, desmetryn and carbofuran, when the ethylene-vinyl acetate copolymer (20% vinyl acetate) formulations were compared with the corresponding wettable powder (wp) formulations, required considerably greater time in the case of the copolymer and indicated which extrapolated release times of the order of weeks or months.

With carbofuran a considerable hydrolytic decomposition of the released substance to the carbofuran-phenol occurred, while the substance remaining in the matrix always could be isolated unaltered. This protection against premature decomposition is of great importance in long term applications.

The extrapolated duration of pesticidal action of the ethylene-vinyl acetate and polyethylene formulations described lasts from several weeks up to years and depends on geometry, surface to volume ratio and temperature.

The properties of these formulations would appear to make them useful depot systems for the application of pesticides in aquatic conditions to control weeds and mosquito larvae, for example  However, as the matrix is not readily biodegraded, they require to be used in a replaceable mode, which should not present undue problems

The possibility of controlling aquatic weeds in running water by means of a cable-shaped EVA/terbutryn formulation of 2 mm diameter has been investigated in a model flow system on a laboratory scale with duckweed (*Lemna minor*) as the test plant  This species provides easy and quick cultivation by vegetative propagation, the age of plants and state of growth can be estimated from the length of the roots, the small size enables large numbers of plants to be used for experimentation, and as they are free floating, these can be likened to other important weed species, such as the water hyacinth (Eichornia crassipes)

In the flow system, nutrient solution was pumped from a storage container at a rate of 0.5 l/h to the first of a sequence of 6 two-litre jars connected to each other by glass tubes in combination with small chambers, containing pieces of the formulation pieces in increasing amounts. In this way, depending on the release kinetics, an increasing gradient of herbicide concentration was formed from jar 2 to jar 6. As a control, jar 1 was kept free of any herbicide.

At the beginning of the experiment 50 duckweed plants of similar vegetative state were added to each jar and exposed to light.

After a period of 12 days the course of the herbicide concentrations could be determined. These varied from 30 ppb (parts per billion, 10-9) up to about 1 ppm (10-6) after 1 day and reached equilibrium values of 10-260 ppb after 1 week. At this time the number of plants in the control jar had increased to 370. In jar 2 only 115 plants were counted, but in all the other jars there was no increase in plant numbers at all. At 12 days, all the plants in jar 3-6 had been destroyed.

The results of this unreplicated experiment indicate that it should be possible to control aquatic weeds under practical conditions using these formulations. As the relatively low concentrations of active agent released can be very effective, when they are applied in a controlled release form, such formulations would avoid contamination of the environment.

## 9.4 Release into Air (Pheromones)

### 9.4.1 Insect pheromones and their application (A.K. Minks)

Pheromones are substances which are secreted to the outside by an individual (animal) and received by a second individual of the same species in which they elicit a specific reaction, for example, a definite behavioural pattern or developmental process.

The potent long-range attraction of particular sex- and aggregation pheromones opens very interesting possibilities for use of these substances in insect pest control.

The following three methods can be used:

a. Detection and monitoring. Pheromone traps have important advantages to other trapping methods as light traps and suction traps.

b. Mass trapping.

c. Mating disruption

The application of pheromone traps for detection and monitoring of insect populations is of great interest for developing countries, because of its simplicity, provided that the pheromone itself is available.

#### Different types of pheromones

Pheromones mediate adaptations in behaviour or physiology, which give the insect more chance of reproductive success or survival. Pheromones belong to the semiochemicals; and chemical which provides for information between organisms. Other terms in use are: behaviour-mediating or behaviour-modifying substances.

### a. Sex pheromones

Sex pheromones provide for communication between both sexes, bringing them together and improving the chance of successful mating. There are two different phases in the act of copulation. The first is mate location; when a chemical mediates long-range location it is called a "sex attractant". After a mate has been located, there is a switch from mate location to courtship behaviour. Courtship is a sequence of behavioural activities by male and female at close-range which co-ordinates their reproductive efforts.

Sex pheromones of moths (Lepidoptera) have been investigated extensively. These are usually multicomponent mixtures.

### b. Aggregation pheromones

A pheromone that releases behaviour in conspecifics leading to an increase in their number in the vicinity of the pheromone sources is termed an aggregation pheromone.

### c. Dispersal or spacing pheromone

This type of pheromone stimulates behaviour that leads to increased spacing between individuals.

### d. Alarm pheromones

Alarm pheromones stimulate escape and other defensive behaviour. In several aphid species, trans-farnesene, released from the cornicles when an individual is attacked by a predator, stimulates nearby aphids to disperse or drop from the plant and escape.

### e. Recruitment or trail pheromones

Trail pheromones are common in social insects, particularly in ants and termites. When food is located by a worker it lays down a pheromone trail as it returns to the colony. Other workers are recruited to the source by following the chemical trail.

## Use in insect pest control

### a. Detection and monitoring

Traps baited with sex pheromones are widely used in practice for detection of certain species in certain areas. These traps are easy to handle and because of their specific action, time consuming sorting and identification of the caught insects can be avoided In addition, simple and cheap materials can be used and no electricity is needed.

Pheromone traps are sensitive at low insect population densities and it is certain that they will catch the first males emerged in the field. This makes this method extremely suitable for detection and delimitation of early infestations over large areas of forest and also in stored-product infestation.

Sex pheromone traps are frequently used to obtain in a simple manner an impression of the actual population density of a certain pest in a certain field. However, pheromone traps catches are always low, because they are a reflection of the number of individuals of the population that exhibits a certain activity pattern after perception of the pheromone and such a response is never shown by 100% of the population.

There are many factors that effect the catches. These include:

| | |
|---|---|
| a. Trap design | factors a-f can be manipulated by the user of the traps |
| b. Pheromone dispensers | |
| c. Pheromone chemicals | |
| d. Trap maintenance | |
| e. Trap replacement | |
| f. Trap density | |
| g. Population density | factors g-k cannot be manipulated, are related to behavioural capacities of the insects |
| h. Response capacity | |
| i. Activity level | |
| j. Competition effect | |
| k. Migration | |

### b. Mass Trapping

The idea of mass trapping with pheromones as a direct control method is to lure away such a high proportion of individuals from a certain population that it has a strong negative effect on the further development of that population. There are many major difficulties which make this simple idea complicated in practice.

### c. Mating Disruption

The second technique of direct control by using pheromones is called mating disruption or male confusion. It is aimed at interfering with premating communication between male and female moths by permeating the air with synthetic female sex pheromones. This is used only for lepidopterous pests. To achieve disruption, it is necessary to disperse the synthetic material as extensively as possible in the habitat of the pest insect and to maintain the aerial concentration at a level sufficient to disrupt mating.

Because of the high volatility of most pheromone attractants, it is necessary to use formulations that can maintain a sufficiently high level for a long time (days or preferably, weeks). Synthetic pheromones can be liberated in a variety of ways ranging from widely spaced dispensers to broadcast spray operations. With this method an even distribution over the crop is obtained and it is ensured that there are few pheromone free areas in which sexual communication between male and female moth will occur.

Formulations that can be broadcast are sprayable microcapsules and dispersable chopped hollow fibres and small laminate flakes. An alternative to dispersable methods is to release pheromones from evenly spaced evaporating stations at such a rate that the amount liberated per unit areas is also the lower threshold for disruption. For this approach there are three systems available.

a. rubber tubes or septa
b. hollow fibre dispensers, made of polyester, open at one end and attached to cards in groups of 20 or more, which can be hung up in the crop.
c. laminated plastic sheets whereby the pheromone reservoir is held between protective plastic membranes through which the pheromone diffuses slowly.

The largest evaluation of mating disruption which also was a modestly commercial success but less so now, has been attempted with the pink bollworm, *Pectinophora gossypiella*, on cotton in the United States, India and South America. Over 50,000 hectares of cotton were treated in 1980 with synthetic pheromone in the hollow fibre formulation. The results, measured by reduction in trap catches, mating of tethered females, development of subsequent larval population and rates of infestation of cotton bolls, were quite successful. But in spite of this success and that achieved in a few other cases, until now progress towards more general application of mating disruption has been slow.

### 9.4.2 Controlled released systems for the delivery of insect pheromones
(B.A. Leonhardt)

To date, pheromones and attractants have been identified for a large number of insects and other arthropods. These include:

| Order | Number of compounds |
|---|---|
| Lepidoptera (moths and butterflies) | 475 |
| Diptera (flies) | 37 |
| Coleoptera (beetles) | 82 |
| Hymenoptera (wasps and sawflies) | 35 |
| Homoptera (scales and mealybugs) | 18 |
| Acarina (ticks and mites) | 14 |
| Others | 13 |

To be effective for pest monitoring and control, a pheromone has to be delivered at sufficient dose levels and for a long period. The specifications for an appropriate controlled release formulation covers:

a. deliver and effective amount of pheromone over an extended period
b. prevent chemical degradation
c. deliver pheromone to the target insect
d. use minimal amounts of lure; be commercially feasible.

Many of the lepidopteran sex attractants are made up of aliphatic aldehydes, alcohols or acetates which have 10-20 carbon atoms and one or more double bonds. Other classes of pheromone compounds include: olefins, methylalkanes, epoxides, esters other than acetates, ketones, phenols, alicyclic alcohols or acetates, spiro compounds, carboxylic acids, chlorinated hydrocarbons. Pheromones are quite volatile, active in very small quantities and are often unstable in air. Most of the compounds are expensive to synthesize since, in many cases, the geometric or optical purity of the compounds must be very high for full biological activity. For these reasons, it is most desirable to use controlled release formulations.

### Reservoir systems

If the pheromone compounds are placed in a container with no barrier to evaporation or are deposited on a substrate such as cigarette filters, or other absorbing materials, this is called a reservoir system. Since there is no polymeric membrane to prevent evaporation, the pheromones are released into the air at rates dependent on the exposed surface and their volatility.

Another example is hollow fibres which contain pheromone Each fibre contains a column of a pheromone solution. The size of the opening at the top of the fibre controls the rate of evaporation.

### Reservoir systems with membrane

If, however, the reservoir of pheromone is covered by a polymeric membrane, this slows and controls the rate of evaporation. The pheromone now must diffuse through the membrane before it can evaporate from the surface. The less porous the membrane the slower the rate of pheromone release. Examples include microcapsules.

Another such formulation consists of a pad as a porous substrate and contains the reservoir of pheromone. A clear membrane prevents the rapid evaporation of the pheromone. Such a bait can remain effective in a trap for several weeks or more. This type of dispenser can be purchased containing the appropriate pheromone for a variety of insects.

### Matrix systems

In the matrix system the active compounds are dispersed or dissolved in the polymer. In some cases the polymer erodes with time and then releases the pheromone as it erodes. Most of the systems, however, are not erodible and the pheromone diffuses through the polymer barrier to the surface where it evaporates. Matrices include a wax with the pheromone dissolved in the wax. Incorporation into polymers can be mixed with the polymer or by suspending in the monomer followed by polymerization. The rubber septum dispenser is an example of the first method. In this case incorporation is achieved by adding a solution of the pheromone in dichloromethane to the hollow of the septum. The rubber is swollen by the solvent allowing the pheromone to penetrate. When the solvent evaporates, the rubber shrinks, entrapping the pheromone which must then diffuse to the surface for evaporation. Release from this type (rubber) of elastomeric matrix follows a logarithmic relationship.

### Laminate systems

In the laminate the top and bottom layers are made of a semi-permeable polymer film or membrane. The inner layer contains the reservoir of pheromone dispersed in a suitable matrix. Over the past 10 years, there has been a great deal of success using these laminate dispensers in traps. For example, small pieces of laminate containing the pheromone of the gypsy moth to bait traps that were attractive for 2 months or longer. In fact, larger pieces of laminate stapled to trees were effective in disrupting mating communication for three years in the gypsy moth programme.

Measurement of release rates

With all the formulations it is essential to measure the release rates before the dispenser can be used in the field. The easiest method is by weight loss. However, the amount of pheromone is usually too low for this method to be used. It is more practical to measure the amount of pheromone remaining after the dispenser has been left in the field for known lenghts of time. Assuming no chemical degradation has occurred, the difference between the original loading and the amount left is then the quantity released.

It is better to measure the amount actually released. A special apparatus housed in a constant temperature oven is used. A stream of air at 100 ml/min is passed over the dispenser and then through a column of solvent; the evaporated pheromone is carried by the air stream and is trapped in the hexane solvent and then analysed by gas chromatography. These techniques can be used to study a wide range of variables in the design and assessment of formulations. For example, for about a $10^{o}$ increase in temperature, we get a 3-7 fold increase in emission rate. Therefore, if a dispenser is used under hot weather conditions, a different formulation is needed compared to that for a cool climate.

### 9.4.3 Development and testing of controlled release pheromones and insecticides (K.L. Smith)

The pheromone used in controlling the pink bollworm, *Pectinophora gossypiella*, by mating disruption, known as gossyplure, is a racemic mixture of 16-carbon, doubly unsaturated acetates, and is somewhat less volatile than many pheromones. However, it is used under hot climatic conditions and therefore controlled release is mandatory for long term efficacy in the field. Formulations have been available for mating disruption for several years. These are limited by a duration of activity of only 10-15 days and a requirement for special equipment for their application.

To overcome these problems, microcapsule and granule systems were investigated. Both formulations basically consist of membrane coated reservoirs, and therefore are capable of constant release. Microcapsules were tested in the field (Arizona, cotton), but results were inconsistent even though the pheromone was released for 40 days. It appeared that the microcapsules disrupted communication at low population densities but not at high. Larger point-sources are required for mating disruption and the mechanism of disruption is "false-trail" following rather tnan saturation or desensitization.

Thus the larger granules were developed. These are about 80% by weight pheromone and have diameters from about 500 um to about 5 mm. The release of pheromone is controlled by diffusion of the pheromone through a polymer layer at the surface much the same as microcapsules, and can therefore be controlled at constant rates. Two sizes of granules were tested in small field tests in Arizona in 1984: 1 mm and 5 mm granules. Both sizes worked well· greater than 95% mating disruption (measured by reduction in trap catch) for longer than 28 days during the hottest month (August) of the seasons in Arizona.

Aerial application with conventional equipment is easily accomplished - a simple replacement of nozzles with open tubes is all that is required. Current larger-scale field test are expected to establish minimum effective doses and season long efficacy.

### Controlled release insecticide products

Controlled release insecticide microcapsules for household insect control were developed in the same manner as were the pheromone microcapsules. The core of the microcapsule consists of pure insecticide and is surrounded by a polymeric wall. Typical microcapsule diameters range from 5 to 50 um. As is the case with pheromones, the release rate is controlled by the permeability of the microcapsule wall and by the size and wall thickness of the microcapsules.

The microcapsules contained naled for use against German cockroaches (*Blattella germanica*). These were tested in an enclosed container and compared with a naled-containing controlled-release collar (Sergeants), and two different commercial microencapsulated insecticides used against cockroaches Sectrol$^R$ (SM Registered Trade Mark) containing, pyrethrins, and Knox Out 2FM$^R$ (Pennwalt Corpn Registered Trade Mark) containing diazinon. Over a 5-month period, the efficacy of the formulations was determined by measuring the time to knock-down 50% of the cockroaches placed in the chamber ($KT_{50}$). The flea collar and Knox Out 2FM microcapsules exhibited almost 3 months' efficacy, while Sectrol microcapsules lost efficacy after just a few days and the naled microcapsules lasted for at least 5 months. Although laboratory release- rate testing has not been performed for the other three formulations, an excellent correlation exists between duration of naled release and duration of efficacy for the naled microcapsules.

### 9.4.4 Utilization of insect pheromones for monitoring populations in IPM programmes (K.V. Raman)

Synthetic pheromones can be used in monitoring insect pests and in pest control by mass trapping and communication disruption. Their use in developing countries has been described by this author and recent work done at the International Potato Centre, Lima, Peru is covered here. This work has been in collaboration with other countries and in particular with chemists from the U.K. Overseas Development Administration's Tropical Development and Research Institute and the Institute for Pesticide Research, Wageningen, The Netherlands.

The major pests of potatoes for which sex pheromones have been identified include: Potato Tuber Moth (*Phthorimaea operculella*), (*Scrobipalpopsis solanivora*), Cutworms (*Prodenia eridana*) and (*Spodoptera exempta*). The female sex pheromone of the Potato Tuber Moth (PTM) (*P. operculella*) one of the most widespread pests affecting potato in field and storage in many parts of the world, consists of two substances. The pheromones of two major cutworm species damaging potatoes are available commercially from the Wolfson Unit of Chemical Entomology, University of Southampton, U.K Other important pests for which pheromones are not yet synthesized include Leafminer fly (*Liriomyza huidobrensis*), Andean potato weevils (*Premnotrypes suturicallus*) and the potato leafminer (*Scrobipalpula absoluta*). Some success has been achieved with *S. absoluta* and *S. plaesiosemus* using virgin females.

Detailed research on pheromone use for potato pests indicated that a suitable funnel trap was a better alternative to the water trap. No significant differences were reported for trap capture of PTM between these two traps. Current trap designs available for evalution in national programmes include funnel, water and sticky traps. Pheromone traps placed in a potato field provide good correlation between oviposition by PTM on the foliage of plants and pheromone trap data. This indicates that when male moths are monitored, the data reflects the ovipositional activity of the female component of the population which is not monitored. Male PTM moth capture is correlated positively with tuber damage at harvest. For effective trapping it is essential to have a pheromone blend which would be attractive for a long period of time, and the cost of the pheromone should be low.

Progress has been made with _P. operculella_. Highest capture was obtained by using a blend of PTM 1 and PTM 2 pheromone in 9:1 ratio. The effectiveness of pheromone blend varies from one location to another and careful experimentation is needed to identify the most attractive pheromone blend. Laboratory techniques to impregnate the pheromones blend in rubber stoppers have been developed. Work has also been conducted on reducing the cost of rubber stoppers by using smaller size (9 mm diameter) stoppers. The cost of the blend would be significantly reduced if these could be used with impurities. Unfortunately, the presence of these impurities reduces trap catch dramatically.

The main emphasis on the use of pheromones in the developing world must initially be on monitoring. In countries where insecticides are used heavily, experiments designed to reduce insecticidal application through monitoring and establishing relationships between trap catches and damage will be useful Additional work is also needed on where pheromone traps need to be placed in an environment. Work at the International Potato Centre suggests that the formulation of pheromones at the national programme level will reduce the cost of this technology. Formulating pheromones using solvents is a very simple procedure, and with training this can easily be conducted in developing countries. The Centre would be willing to share its experience with any national programme interested in this area of research.

### 9.4.5 _Use of pheromones and other attractants in programmes aimed at tsetse fly control_ (D.A. Carlson)

a. Transfer male-produced cuticular alkenes and radiolabelled alkanes of females. An understanding of the reasons for the existence of male-specific compounds from the cuticle in female tsetse flies was sought. This would help in determining the possibility of whether field caught females had mated.

b. Use of the sex pheromone of _Glossina m. morsitans_ combined with bisazir, a chemosterilant. At present, insecticide treated targets are being employed successfully in Zimbabwe for population suppression of _G. pallidipes_ and _G. morsitans_ by Dr. Vale. The targets kill both sexes, and placement of sufficient targets to kill 1% of the population per day is probably as economical as ground spraying with insecticides.

However, the nylon fabric materials used originally in Zimbabwe required daily treatment with bisazir (BA) to achieve good activity. This was satisfactory for a demonstration, but suggests the need for slow release formulations. Our previous work has shown relatively high vapour pressure for BA of about 0.005 mm Hg at 25°C. This indicates relatively rapid loss of BA without the benefit of a good formulation, and this was observed.

In the laboratory it was observed that mated female flies exposed to 500 mg of BA absorbed on to 10x10 cm rubber sheets were completely sterilized in less than 24 h. The rubber sheet was effective at one week, but less effective after 2 weeks and inefficient at 4 weeks. Also, males were seen to be slightly less sensitive than females.

c. Other attractants for biting flies. 1-octen-3-ol is an olfactory stimulant for _G. morsitans_ as shown by an electroantennogram technique. This material was discovered in ox odour. It is a potent attractant in field dispensers which consist of small glass vials containing up to 5 ml, covered with a rubber septum. The septum was kept wet by contact with a folded pipe cleaner whose lower end was immersed. Dispensing rates were 9 mg per day for 60 days. Another dispenser was a thin polythylene vial containing up to 100 mg of 1-octen-3-ol plus 600 mg of paraffin oil. The heat-sealed vial released 0.4 mg per day.

Compared to ox odour, the mixture of carbon dioxide (2 l per minute), acetone (5 mg per hour), and 1-octen-3-ol (0.05 mg per hour) attracted 83% as many _G. morsitans_ and 46% as many _G. pallidipes_. However, even 10 times more of each chemical was released, capture of flies was about double those of an ox. It is not too early to test slow release concepts for materials like these, although quantities are large for some of the chemicals. However, these existing results are impressive.

## 9.5 Veterinary Applications

### 9.5.1 Controlled release delivery systems for control of external parasites of livestock (F.W. Knapp)

We have very few pesticide delivery systems in livestock entomology which release their contents in a controlled release fashion, rather, most are considered to be slow release. The technology is available to construct slow release pesticides of all types to meet our every demand and at the same time, protect our environment by using less pesticide.

It is difficult to differentiate between medical and veterinary entomology, as some pests attack both man and animals. Therefore, some aspects of medical entomology have to be considered. Slow release pesticide delivery systems for medical entomology tend to be limited to the control of mosquito larvae. Chemicals now being utilized in slow release systems are chlorpyrifos (Dursban R) and temephos (Abate R) and diflubenzuron (Dimilin R) both of which are insect growth regulators

Dursban controlled release (CR) granules will give effective control of mosquito larvae for a period of several months to a year. A slow release formulation of temephos is now commercially available with a life expectancy of 7 years. The formulation of methoprene Altosid$^{(R)}$ charcoal briquets originally only gave 30 days effective control of the larvae of certain species of mosquito, but improvements have extended efficacy from several weeks to months.

Dimilin has shown great promise for mosquito control but breaks down rapidily in water. A formulation using urea-formaldehyde has been developed that is effective for 1 year. If diflubenzuron can be cleared for mosquito larval control this formulation can be cleared for mosquito larval control this formulation would be beneficial. Also the promising new microbial insecticide, *Bacillus thuringiensis* var. *israelensis* known as Bti is now being incorporated into slow release formulations and is reported to give 30 days or more control.

A common insect repellent, deet (*N*,*N*-diethyl-*m*-toluamide) has been encapsulated, and this extends efficacy from a few minutes to several hours. This should prove very useful extending the effectiveness of other mosquito repellents for humans as well as livestock.

The greatest advance in slow release for pest control has been in veterinary entomology. Vast improvements have been made in pest collars for flea and tick control so that today the average life of such a collar is about 5 months. However, a PVC-chlorpyrifos collar has been developed with label claims for control of fleas and ticks for 11 and 10 months, respectively. A collar is available that contains two pesticides, naled and propoxur.

Slow release ear tags have been developed to give season-long control of insect pests of livestock, particularly horn flies, in the USA and elsewhere. The first commercially-produced insecticide impregnated cattle ear tag for fly control were based on the organophosphate, tetrachlorvinphos (Rabon$^{R}$). However, the pyrethroid tags have revolutionized livestock pest control methods. These tags can be applied to cattle during the early spring and give 60 to 80% reduction of face flies, (*Musca autumnalis*), and almost 100% control of horn flies for 20 to 24 weeks. Ear ticks (for example, *Otobius megnini* and *Amblyomma maculatum*) are also controlled by these tags. There are a variety of tags, in different shapes and colours and contain mainly permethrin (Atroban $^{R}$), fenvalerate (Ectrin$^{R}$), and flucythrinate (Guardian$^{R}$).

A recent method uses a tape, containing two ampoules of technical grade permethrin (1 gram in each) which is attached to an existing ear tag or around the tail of an animal. The ampoules are then ruptured by finger pressure. The permethrin is absorbed in a wick-like material and thus acts as a slow release mechanism. Excellent horn fly and good face fly reduction are archieved.

The impregnated ear tags were at first very effective against the horn fly and fairly active against the face fly. Data has shown weaning weights of calves to increase as much as 0.01 to 0.02 kg/head per day. The use of these tags in areas where face flies are present has helped reduce the incidence of infectious bovine keratitis in cattle.

However, after about three years use, horn fly resistance to pyrethroid ear tags appeared in the southern part of the USA. In some areas, multiple resistance was noticed with the organophosphate, tetrachlorvinphos. Horn fly resistance has now spread northward to around the 40th parallel. Thus far only the horn fly has become resistant as a result of ear tag use on livestock in the states of Oklahoma, Texas, California, Georgia, Kentucky, Kansas, Nebraska, Hawaii, Mississippi and Louisiana.

Ear tags are being improved to try to overcome this problem. Several tags now contain a combination of organophosphate and pyrethroid insecticides. The rate of release from the tag may be a problem. Research on the rate of release of pyrethroids showed a rapid release over the first few days. Horn flies started returning to the cattle after 20 weeks. At the end of this 30 week test, more than 50% of the pyrethroids were still in the tag. If the release rate profile could be improved, less pesticide would be needed, thus reducing the cost and also possibly delaying the onset of resistance.

Another slow release mechanism used for fly control is aimed at flies breeding in dung. A large pill, called a bolus, usually weighing about 50 gram and containing 10 to 20% of a pesticide is given orally to the bovine animal. With an applicator the bolus is placed in the recticulum of the first stomach of the animal. The release of the pesticide is accomplished by erosion and can last for 90 to 120 days. Usually the dosage is one 59 g bolus per 250 kg of body weight. Calves usually receive 1/2 of a bolus. When more than one is administered, movement of the boluses against each other increases the release rate. Enough of the pesticide is released to control the larvae breeding in the animals droppings or dung. When the bolus is reduced to about 5 gram, the whole bolus is released from the body. This approach is based upon insect growth regulators aimed at the fly pest. These include diflubenzuron, methoprene and triflumuron.

Insecticide feed-through, although not in the category of slow release, work in a similar manner, i.e. the livestock daily consumes a small amount of pesticide in its ration or mineral. These feed-throughs are usually directed towards control of insects breeding in the animal faeces although some are also directed towards blood-sucking pests and intrnal parasites such as the cattle grub (Hypoderma sp.).

New pesticides will continue to be discovered and will be a future part of livestock pest control. However, the effectiveness of a pesticide is only as good as the delivery system. Slow release systems will continue to be an important phase of insect control on livestock and crops if they provide a more efficient and safer use of pesticides.

### 9.5.2 Controlled-release formulations in animal production (H. Jaffe)

In addition to the delivery systems outlined in the previous section, is the method of implantation. Particularly important in livestock are implants for the delivery of animal-systemic compounds such as insect growth regulators (IGRs) or insect steroid hormones (ecdysteroids) into the circulatory system of the host animal to affect feeding parasites of the livestock

Polymers used for the implantation approach need to be compatible with the host and include biodegradable polyesters such as poly(lactic acid), poly(glycolic acid), poly(caprolactone) and their copolymers

Both matrix and reservoir systems (see Section 1.4) have been developed for the juvenile hormone analogues or insect growth regulators, methoprene and A13-36206. Microcapsules and pellets, of the IGR in a matrix were prepared. Microcapsules were prepared by an emulsification-solvent evaporation method.

To a stirred solution of surfactant in water was added a dichloromethane solution of the polymer and the active agent to form an emulsion. Continued stirring and evaporation of the non-aggregated microcapsules.

Pellets were prepared by dissolving both the polymer and the IGR in dichloromethane. Complete removal of the solvent gave a film. Pieces of film placed in teflon tubes were compressed by application of pressure applied by glass rods at 54–55$^{o}$ to form pellets.

Pellets and reservoir devices, and also the microcapsules were implanted in the ears of cattle using the standard Synivex veterinary implanter. The release rates were measured in vitro. With the microcapsules and pellets a rapid release occurred during the first 10 days followed by a near linear rate for the next three months.

Experiments were run designed to evaluate the practicality of our implants and their efficacy against the cattle grub,(Hypoderma lineatum), an insect whose larval stage migrates through the body of the cattle Animals infested with cattle grub were implanted and the larvae were collected as they emerged from the host's back and allowed to pupate The experiments on cattle grubs demonstrated the feasibility of using both types of systems, matrix and reservoir, for the control of arthropod pests of livestock throughout an entire season with only one treatment. A matrix, based on polylactic–glycolic acid, gave short-term (1–2 months) control. The polycaprolactone reservoir devices are promising for use as a long-term (1 year) controlled release system.

Both reservoir and injectable microcapsule formulations of the ecdysteroid IGR have been prepared and have shown promise when evaluated against the camel tick (Hyalomma dromedarii) on the rabbit.

In summary, the ability to deliver very potent compounds such as juvenile hormone and logues or ecdysteroids via an implant in the host has important implications for future control strategies.

9.5.3 An intra-ruminal device for controlled infusion into the fore-stomach of free ranging animals (K.J. Ellis, P. Costigan, A.C. Schlink)

The description and uses of a variable geometry controlled release device for ruminant animals is described. This was based on work orginating from Dr. R. Laby of the CSIRO Division of Animal Production. In this device the active material released is dispersed in a solid core of matrix which is contained in a cylindrical barrel with an opening at one end. When immersed in an aqueous environment of the rumen, water penetrates the core at the orifice resulting in a viscosity change and/or dissolution, depending on the particular formulation. A compressed spring at the opposite end of the core serves both to keep the core pressed against the orifice and to bring about some extrusion of the wetted or swollen matrix. This extruded material is relatively fluid, and is quickly dispersed by rumen motion. Since water uptake can only occur at the orifice, the area of matrix exposed to rumen liquor is constant and a dynamic equilibrium is quickly established resulting in a linear release profile. Release lifetimes can be varied from a few days to months, by changing the spring or matrix characteristics.

Retention of the device in the rumen is achieved by the pair of flexible "wings" at the end of the barrel. These are aligned along the barrel during dosing but then open to produce a "T" shape once in the rumen. In practice, a single sized device was found suitable for sheep, calves, goats and fallow deer.

Applications include the constant delivery of faecal and digest markers (e.g. chromic oxide), delivery of tracer elements for feed supplementation or diagnosis of trace element defiencies, and delivery of growth promotants and anthelmintics. The nature of the device allows for reliable and known treatment under range conditions with infrequent dosing.

## 9.6 Potential Applications of Controlled Release in the Tropics

### 9.6.1 Present and potential uses of controlled release agrochemicals in Lebanon (N.S. Kawar)

Agriculture plays an important role in the economy of Lebanon and crop production is quite diversified. Along the narrow coastal strip, the main crops are citrus, bananas, vegetables and tobacco. In recent years, a large number of plastic houses were set up in this strip for the production of a variety of vegetables, flowers, strawberries. At elevations ranging between 200 and 600 m above sea level, deciduous fruits, especially apples and pears, are the predominant crops. The Beka' plain, which comprises the main agricultural area of Lebanaon, has an elevation of about 1000 m above sea level. In this region, cereals, sugarbeet, vegetables, grapes and stone fruit are grown

The Lebanese farmer has always been very receptive to the idea of new technology in crop production, especially the use of agrochemicals. Consequently, the application of pesticides became widespread to the point of excessive use or abuse, in many instances. This resulted in pesticide residues in crops exceeding the permissible level on one hand, and the appearance of resistant strains of pests on the other. Plant protection specialists in both the private and public sectors have realised this and are trying to develop appropriate strategies.

Controlled release agrochemicals have been introduced into Lebanon and are being used on a limited scale. Examples of these applications include the use of attractants in poison baits for the control of the olive fly, (Dacus oleae), and the mole cricket, (Gryllotalpa gryllotalpa), which is a very serious pest of vegetables and field crops. Pheromones are being used for monitoring the codling moth, (Laspeyresia pomonella), on apples and the Mediterranean fruit fly, (Ceratitis capitata) on citrus. However, these applications have been limited to small scale operations by individual farmers and no nation-wide projects have been started until recently.

Early in 1984, a group of plant protection specialists from the Ministry of Agriculture, the Lebanese National Council for Scientific Research and the American University of Beirut started setting up plans for an extensive plant protection research project. It will involve studies of the pests of the major crops, current methods of control, and the introduction of new concepts of control including the use of pheromones and controlled release formulations.

### 9.6.2 Pest and disease problems and management practices in root field crops in Nigeria (U.G. Atu)

Of the major tropical root crops, cassava, yam, sweet potato, and cocoyams are the most important in Nigeria. Cassava and yam are the most widely grown. These two crops provide about 75% of food calories with yam accounting for 50%, as it is a better dietry food. Traditionally, yam is also a prestige crop and a man's wealth used to be assessed by the size of his yam barn. However, cassava is hardier, cheaper and easier to grow Also in some areas of Nigeria, the sweet cassava, with low hydrogen cyanide content in the tuber flesh, can be boiled and eaten like yam. These factors account for the wider distribution of cassava than any other root crop in Nigeria.

All the four root crops, except sweet potato, stay from seven to fifteen months in the field before harvest. They are therefore exposed to many more pests, which reduces yield and crop quality.

The major pests identified to attack cassava are: the cassava mealybug (*Phenacoccus manihoti*); green spidermite (*Mononychellus tanajoa*); red spidermite (*Oligonychus gossypii*); variegated grasshopper (*Zonocercus variegatus*); white fly (*Bemisia tabaci*). Of these only cassava mealybug, green spidermite and occasionally variegated grasshopper currently cause economic damage.

Yam pests that can cause economic damage in Nigeria are: yam beetle (*Heteroligus meles*); yam nematode (*Scutellonoma bradys*); root-knot nematode (*Meloidogyne* spp.); crickets (*Gymnogryllus lucens*); termites (*Amitermes evuncifer*); scales (*Aspidiella hartii*); mealybug (*Planococcus citri*) and yam tuber borers (*Decadarchis miniscula* and *Araecerus fasciculatus*).

Control of these pests, and others such as pathogens and weeds is largely based on management. In addition, biological control has been attempted. The use of foliar applications of a range of insecticides as well as soil treatments by systemics such as carbofuran are used where appropriate.

However, losses in these root crops are high The long growing season during which the crop is in the ground, combined with the high moisture content of the tubers, makes them very susceptible to attack. This damage may not be appreciated until the crop is in storage when considerable losses occur. Over one million tons of yam are lost in storage annually in West Africa.

Effective control of the field pests of tubers would increase the storage life, although some form of processing (flour or chips) may reduce losses. Avoidance of wounds on tubers during harvesting and handling would also reduce storage losses. Under tropical conditions, pesticides breakdown and become ineffective rapidly, a particular problem in the case of protection of the long-season root crops. Repeat treatments would increase the costs and thus this is an area where controlled release could play an important role. In addition this approach would harmonize with many of the principles of integrated pest management, which is very much in the formative stage in respect to these root crops.

### 9.6.3 Preliminary characterization of a lysozyme sensitive bioemulsifier active against organophosphorus pesticides (M.N. Patel, K.P. Gopinathan)

Bacterial strains have been isolated that are capable of very rapid emulsification of water-insoluble lipophilic organophosphate insecticides. The bioemulsifier which is secreted by the bacteria during pesticide dependent growth and not during growth on glucose appears to be high molecular weight non-dialysable glycolipid that is stable up to 120°. It also appears to be specific for organophosphates and is sensitive to digestive enzymes, lysozyme, lipase, protease, cellulase, etc. This material, when isolated could have potential for removal and degradation of pesticide residues. Because it is labile and highly active there is also the potential to exploit it in controlled delivery systems of these insecticides.

## 9.7 Using Isotopes in Controlled Release Technology

### 9.7.1 The use of an aquatic microecosystem to evaluate the bioavailability of carbofuran applied as a controlled release formulation (C. Pascucci, A. Isensee)

The use of a laboratory microecosystem is the ideal tool for an investigation on the influence of parameters, such as different formulation types, on the fate and persistence of a pesticide in soil and water and its bioaccumulation in non-target organisms. A laboratory microecosystem effectively integrates many environmental processes into one experiment, and combines the effects of several variables acting simultaneously. It facilitates the use of radiolabelled compounds. The labelled compound is contained in alose system and can be easily disposed of with little chance of environmental contamination. Only small quantities of these expensive materials are needed. Radioisotope techniques can integrate effectively the normal analytical methods in the analysis of pesticide residues in the different parts of the ecosystem.

This investigation was undertaken to determine how a controlled release formulation of carbofuran applied to the soil in an aquatic microecosystem affected losses into water, persistence in water, and bioavailability to mosquito, fish and to daphnids.

Radiolabelled formulations. Alginate gel formulations of carbofuran were prepared from sodium alginate solutions using $^{14}$C-labelled carbofuran. Barium chloride solution was used as a gellant and synthetic latex as a formulation filler.

Microecosystem chambers. A microecosystem chamber was prepared to evaluate the influence of formulation type on the fate of carbofuran in soil, water and fish in a simulated aquatic environment. Glass chambers (40x20x25 cm) were constructed with a 6 cm high glass partition located in the center of the tank. The experiments were set up by placing 0.75 kg untreated Matapeake silt loam soil uniformly into one of the equal sized chambers. The untreated soil was moistened to field capacity (26% w/w). A final 235 g layer of soil, treated with carbofuran at the predetermined application rate (0.75 kg a.i./ha.) was added and also moistened to 26%.

Three carbofuran formulations were used: alginate gel granules, unformulated technical grade, and commercial Furadan$^{R}$ 15G granules.

The first two contained radiolabelled carbofuran. Two replicates of each treatment plus controls were used.

After the treated soil has been placed in the chambers, they were flooded with 8 liters of water. One day after flooding, mosquito fish were added to each tank. Daphnids were added to a 1-liter capacity glass tank partially suspended immersed in the water. An opening in the tank bottom was covered with a stainless steel screen to restrict daphnid passage and protect them from predation by the fish. A percolator water pump continuously circulated water into the daphnid tank ensuring uniform mixing of the water. Due to unexpected mortality (treated and control chambers) daphnid samples were introduced into the microecosystem three times during the first 15 days and sampled at day 1 and 3 after introduction.

Two fish samples were taken at days 1, 3, 7, 14 and 30. Water samples (3x1 ml) were taken at regular intervals for total $^{14}$C analysis. At days 3, 7, 16, 30 larger water samples (100 ml) were taken for extraction and analysis by HPLC.

Results from analysis of the water indicated a rapid increase in the carbofuran concentration for the unformulated material and Furadan granules, but a slower increase for the alginate gel and a longer persistence. This showed that $^{14}$C-carbofuran was still being released from the alginate formulation to the soil and then to the water 15-30 days after flooding and thus demonstrating extended release.

The reduced availability of carbofuran in the water in the alginate treatments was reflected in the amount of extractable and unextractable radioactivity in the fish (less than half of that from the unformulated treatment). The radioactivity in the daphnids increased with time but more was accumulated, relative to the water concentration, in the case of the alginate than in the case where unformulated radiolabelled carbofuran was applied.

### 9.7.2 Use of isotopes in pesticide research (M.S. Al-Badry)

A wide range of pesticides are used in agriculture and public health in Iraq. In developing countries, such as Iraq, a growing reliance on pesticides is expected due to shortage of labour and demands for improved agricultural quality and increased production. The use of radioisotopes can help in understanding the interaction of pesticides with living organisms and the environment. For any particular pesticide, investigation could include:

a. uptake and absorption into living organisms.

b. penetration of the skin of, distribution in, sites of action in arthropods and mammals.

c. metabolism.

d. excretion or elimination of the toxicant or its metabolites.

e. fate (movement, degradation) of the pesticide in the environment and potential accumulation in living and non-living organisms.

f. identification and quantification of compounds in the above schemes using radioisotopes.

### 9.7.3 Studies on the residues of 14C-BHC in rice plants and paddy soil and their correlation (Z-Y. Chen, J. Sun, Y-X. Zhang)

BHC or HCH (hexachlorocyclohexane) has been one of the widely used insecticides in the developing world. It is known for its persistence. The aim of this work was to evaluate the environmental safety of HCH and provide a scientific basis for controlling pollution by HCH.

In this experiment HCH, $^{14}C$-labelled in the ring was applied in emulsified benzene solution to field paddy soil contained in beakers, with or without growing rice plants. Alternatively the HCH emulsion was added to pure water contained in beakers. At intervals after setting up the experiment, the water, soil, or river leaves or roots were radiocounted, in the case of the liquid samples by scintillation counting, or after combustion, in the case of the rice plant samples.

Results were obtained in terms of the total radioactivity, i.e. parent labelled material and all carbon-containing metabolites. Organosoluble residues in soil showed a decline with time, reducing to 0.82 ppm after 46 days. Bound residues remained more stable during the experimental period, but also reducing to 0.87 ppm by the 46th day. The ratio of radioactivity in shoots or roots to that in the soil became larger with time.

The loss of radioactivity from water was much greater than that from soil ("relative" concentrations of 0.48 in water to 1.45 ppm in soil at 30 days after application). This rapid loss might occur as a result of co-distillation with the water.

### 9.7.4 Seed dressing with controlled release formulations: preparation and evaluation using radioisotope techniques (B.C. Schiffers, J. Fraselle, M. Gasia, P. Dreze)

The benefits of seed dressing are potentially considerable: the localization and reduction in the amounts of pesticides needed, within the limitations of available pesticides, and combining the two operations (seeding and treatment) into one.

Seed dressing was done in a rotating sphere of copper or stainless steel. To the moistened seeds were added alternatively an aqueous solution of an adhesive and a dry mixture (clay, silicates, sawdust, etc.) with one or more adhesive materials. Further drying will reduce excess water. Water-soluble adhesives, such as polyvinyl alcohols or similar, combine on drying and create a network of films around the active material.

To the seed coating process was added a concentrated suspension of carbofuran (Curaterr SC 330) containing tritiated carbofuran. This was done by preparing a solution of tritiated carbofuran (specific activity: 15.5 uCi/mg or 574 kbq/mg) in acetone with a concentration of 3.22 mg/ml. The tagging of 3.03 g of concentrated suspension (at 33%) is achieved by adding 1 ml of the radioactive solution, which results in about 2 mg of carbofuran per seed. The seed dressing is then finished with talc, wax, paraffin, etc. and coloured using ferric oxide, rhodamine B, brilliant green, etc.

The amount of the seed coating varies, depending on the species and the requirements between 10 and 200% of the seed weight. An average would be 20–30%.

A typical coating for beans would be:

| | |
|---|---|
| – montmorillonite (bentonite) | 50% |
| – amorphous silica | 30% |
| – vermiculite | 10% |
| – adhesive | 10% |

(total is 30–35% of the seed weight)

Standard washing test. To evaluate the release performance of the seed coating, a standard washing test was used. This involved placing the seeds on a bed of sand in a Büchner funnel, retaining water in the funnel for 24 hours and then draining off. The eluate is then mixed with a scintillation fluid and the radioactivity measured by counting. At the end of the test activity remaining in the seeds and the sand was measured.

The results from this type of evaluation indicated that the rate of release was constant for 200 hours after which it decreased slowly. The incorporation of carbofuran in the polymeric seed coating prevented, in the field test, the development of stem nematode in the plant tissue for four months. Yield increases of bean were 8–15% in cases of severe nematode attack. The protein content and the 1000–grain weight were increased. This use of carbofuran controlled release coating is most profitable when combined with crop rotation.

### 9.7.5 Other uses of isotopes in the evaluation of controlled release formulations

Other examples of the use of isotopes to monitor the release of bioactive agents from formulations includes release from pellets made of polyethylene (pretreated with benzene), kaolin and talc (for further details refer to section 9.1.1.) This type of formulation was prepared containing $^{14}$C–labelled carbofuran. Release was determined by a radioassay of the immersion water every week for a period of 8 weeks. About 80% of the label was released nearly uniformly in eight weeks.

In another example, release of endosulfan from alginate gel formulations was studied with the help of isotopes (see Section 9.2.1). Various climatic conditions were simulated in the laboratory to evaluate the release kinetics and protection afforded by this formulation. Analysis of this insecticide is complicated because there are two isomers, one more volatile than the other. Normal analysis was performed with gas chromatography (gc) using an electron capture detector. To detect hydrophilic degradation products high performance liquid chromatography (hplc) was used. The detection limits for gc analysis were 1–10 picogram and for hplc were 1–200 nanogram. However, using $^{14}$C–labelled endosulfan (mixture of isomers; specific activity 12.6 mCi/mmol) the detection limit was not given.

## 10. BIBLIOGRAPHY

Controlled Release Technologies: Methods, Theory and Applications, Vols 1 and 2, A.F. Kydonieus (ed), 1980, CRC Press, Boca Raton, FL, USA.

Controlled Release Technology: Bioengineering Aspects, K.G. Das (ed), 1983, Wiley-Interscience, NY, USA.

Controlled Release Pesticides, H.B. Scher (ed), ACS Symposium Series 53, 1977, Amer. Chem. Soc., Wash. D.C., USA.

Controlled Release Pesticide Formulations, N.F. Cardarelli, 1976, CRC Press, Cleveland, USA.

Controlled Release Polymeric Formulations, D.R. Paul and F.W. Harris (eds), ACS Symposium Series 33, 1976, ACS, Wash. D.C., USA

Controlled Release of Biological Active Agents, A.C. Tanquary and R.E. Lacey (eds), 1974, Plenum, NY, USA.

Controlled Release of Bioactive Materials, R. Baker (ed), 1980, Academic, NY, USA.

Sustained and Controlled Release Drug Delivery Systems, J.R. Robinson (ed) 1978, Dekker, NY, USA

Controlled Release of Pesticides and Pharmaceuticals, D.H. Lewis (ed), 1981, Plenum, NY, USA.

Proceedings of BCPC Symposium on Persistence of Insecticides and Herbicides, 1976.

Microencapsulation Processes and Applications, J.E. Vandegaer, 1974, Plenum, NY, USA

Insect Suppression with Controlled Release Pheromones, Vols. 1 and 2, A.F. Kydonieus and M. Beroza (eds), 1982, CRC Press, Boca Raton, FL, USA.

Formulation of Pesticides in Developing Countries, UNIDO, United Nations, NY, USA.

Pesticide Formulations and Application Systems, Third Symposium, T.M. Kaneko and N.B. Akesson (eds), 1983, ASTM, Philadelphia, PA, USA.

Laboratory Training Manual on the Use of Nuclear Techniques in Pesticide Research, Technical Reports Series 225, 1983, IAEA, Vienna, Austria.

Biopolymeric Controlled Release Systems, Vols. 1 & 2, D.L. Wise (ed), 1984, CRC Pub.

Proceedings of International Symposia on Controlled Release of Bioactive Materials, 1-12., 1974-1985.

## 11. SOME COMMERCIAL CONTROLLED RELEASE AGROCHEMICAL FORMULATIONS

### 11.1 Controlled Release Pesticides (F.W. Harris)

An overview of commercial and semicommercial controlled release pesticides was presented. This focussed on applications in agriculture, particularly for insect and weed control in crops. Specific examples included suSCon$^R$ 140G chlorpyrifos dispersed in plastic pellets; Penncap-M$^R$, a microencapsulated methyl prathion; Disrupt$^R$, insect pheromones in multilayer plastic laminates; and Lasso$^R$ M.E., a microencapsulated alachlor. Controlled release formulations have also been applied to livestock and include Paratect$^R$ anthelmintic, morantrel tartrate, enclosed in a stainless steel tube; and Ectrin$^R$ Ear Tags, fenvalerate dissolved in polyvinyl chloride.

Non-agricultural applications were also surveyed. Controlled release systems for the control of mosquitoes, cockroaches, fleas and ticks, disease-bearing snails, aquatic weeds, and marine-fouling organisms were described. Specific examples included Dursban 10CR$^R$, chlorpyrifos dispersed in chlorinated polyethylene; Knox Out$^R$ 2FM, microencapsulated diazinon; Sentry V$^R$, propoxur and naled dissolved in polyvinyl chloride; Biomet-SRM$^R$, IBTO dissolved in natural rubber; 2,4-D/PolyGMA adducts, 2,4-D chemically attached to polyglycidyl methacrylate, and SPC-40$^R$ Paint, organotins chemically attached to polyacrylates.

#### 11.1.1 Some examples of controlled release agrochemical products

The following list is by no means complete, but indicates that a number of controlled release systems to have achieved commercial status. These are listed according to the formulation type, rather than the delivery pathway.

MICROENCAPSULATION:

| Product Trade Designation | Active agent | Polymer | Application | Company |
|---|---|---|---|---|
| Penncap-M | methyl parathion | polyamide | insect control | Pennwalt |
| Knox Out 2FM | diazinon | poyamide | indoor insects | Pennwalt |
| Penncap-E | ethyl parathion | poyamide | insect control | Pennwalt |
| Micro-Sect | synergised pyrethrins | | indoor insects | 3M |
| Cap-Cyc | chlormequat | | plant growth regulator | 3M |
| Fox-Hyd | warfarin | | rodent control | Warf Int |

| Product Trade Designation | Active agent | Polymer | Application | Company |
|---|---|---|---|---|
| Capsolane | eptam + R25788 | | herbicide + protectant | Stauffer/ Rhone-Poulenc |
| Dyfonate MS | fonofos | | soil insecticide | Stauffer |
| Fulkil | methyl parathion | | insecticide | Rhone-Poulenc |
| Lasso ME | alachlor | | soil herbicide | Elanco |
| Actellic M20 | pirimiphos methyl | | filter bed fly control | ICI |
| Pectimone | gossyplure pheromone | polyurea | insect mating distribution | ICI |

MATRIX SYSTEMS:

| Product Trade Designation | Active agent | Polymer | Application | Company |
|---|---|---|---|---|
| Suscon 140G | chlorpyrifos | polyethylene + "porosigen" | soil insecticide | Incitec |
| Dursban 10CR | chlorpyrifos | chlor-poly ethylene | mosquito larvicide | Dow |
| Ecopro 1700 | temephos | p-ethylene + $CaCO_3$ | larvicide | Environ. Chems. |
| Ecopro | tributyltin fluoride | p-ethylene eth.vinyl acetate copolymer | molluscicide | Environ. Chems. |
| BioMet SRM | tributyltin | rubber | molluscicide | M&T Chems |
| Ecopro 1000 | copper sulfate | ethylene-propylene copolymer | molluscicide | Environ. Chems. |
| Incracide E51 | copper sulfate | p-ethylene elastomer | molluscicide | Int.Copper Res.Inst. |
| 14 ACE-B | 2,4-D | rubber | herbicide | Creative Biol.Lab |
| Reforest-Aid | 2,4-D | kraft lignin | | |

| Product Trade Designation | Active agent | Polymer | Application | Company |
|---|---|---|---|---|
| Midstream | diquat | alginate gel herbicide | aquatic | Albright & Wilson |
| Gridballs | hexazinone | large pellets | range weed | DuPont |
| Dog/cat collars | various | Plasticized PVC, etc. | ectoparasite control | Many |
| Plastic strips | dichlorvos, etc. | PVC, etc. | flying insect control | Many |
| Ear tags | pyrethroids & others | Plasticized PVC, etc. | livestock insect control | Many |

MACRO-RESERVOIR SYSTEMS:

| Product Trade Designation | Active agent | Polymer | Application | Company |
|---|---|---|---|---|
| Hercon | pheromones, insecticides & others | laminate | insect traps insect control | Hercon |
| Biolure | pheromones | membrane | insect traps | Consep |
| Conrel | pheromones | hollow fibers | traps, mating disruption | Albany |
| Paratect | morantrel tartrate | cylinder + membranes | livestock growth stim. | Pfizer |
| Polytrap | liquids | porous polymers | various | Wickhen |

## 12. SUMMARY OF FORMULATION TYPES DESCRIBED AND DEMONSTRATED AT THE MEETING

During the final two days of the Seminar, a number of controlled release formulations were demonstrated including a practical workshop which was held in the laboratory of the Agrochemicals and Residues Section, Seibersdorf. Biolure pheromone devices for insect traps (K.L. Smith and B.A. Leonhardt), the Polytrap System for fragrances and other volatiles in powder, film or membrane form (supplied by S. Barzin) and chemical and physical formulations prepared by K.G. Das.

In addition, a number of formulations were prepared in the laboratory. These included the following:

Microcapsules for injection into livestock (H. Jaffe). This involved the addition of a dichloromethane solution of the insect growth regulator and the polymer (biodegradable polyester) to a surfactant solution. Continued stirring and evaporation provided the microcapsule suspension.

Extrusion of pesticides in thermoplastic polymers (G. Pfister, M. Bahadir, F. Korte). A laboratory set-up using a gas pressurized press and an extruder made from a heated sodium press was demonstrated.

Alginate gel formulations (L. Vollner, C. Pascucci, H. Perschke). Sodium alginate containing endosulfan was crosslinked using calcium chloride on the dried film.

Biodegradable lignin formulations (R.M. Wilkins). By melting the pesticide, kraft lignin may be dispersed in it producing a thermoplastic matrix. Such material could be then extruded or cast to provide granules or other shaped devices.

# Appendix I

## CHEMICAL NAMES OF PESTICIDES REFERRED TO IN THE REPORT

| Pesticide Designation | Chemical Name |
|---|---|
| ATRAZINE | 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine |
| BISAZIR | *P*,*P*-bis(1-aziridinyl)-*N*-methylphosphinothioic amide |
| CARBOFURAN | 2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate |
| CHLORFENVINPHOS | 2-chloro-1-(2,4-dichlorophenyl)ethenyl diethyl phosphate |
| CHLORIDAZON | 5-amino-4-chloro-2-phenyl-3-(2H)-pyridazinone |
| CHLORPYRIFOS | *O*,*O*-diethyl *O*-3(3,5,6-trichloro-2-pyridyl) phosphorothioate |
| 2,4-D | (2,4-dichlorophenoxy)acetic acid |
| DDVP | 2,2-dichlorovinyl dimethyl phosphate |
| DESMETRYN | 2-(isopropylamino)-4-(methylamino)-6-(methylthio)-*s*-triazine |
| DIAZINON | *O*,*O*-diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate |
| DICHLOBENIL | 2,6-dichlorobenzonitrile |
| DIFLUBENZURON | *N*-[[)4-chlorophenyl)amino]carbonyl]-2,6-difluoro benzamide |
| DIQUAT DIBROMIDE | 1,1'-ethylene-2,2'-bipyridylium dibromide |
| ENDOSULFAN | 6,7,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide |
| FENVALERATE | cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate |

| | |
|---|---|
| FLUCYTHRINATE | (±)-cyano(3-phenoxyphenyl)methyl (+)-4(difluoromethoxy)-α-(1-methylethyl)benzeneacetate |
| LINDANE | 1,2,3,4,5,6-hexachlorocyclohexane, *gamma* isomer if not less than 99% purity |
| METHOPRENE | isopropyl (*E*,*E*)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate |
| METOXURON | *N*-(3-chloro-4-methoxyphenyl)-*N*,*N*-dimethylurea |
| MONOLIMURON | 3-(*p*-chlorophenyl)-1-methoxy-1-methylurea |
| NALED | 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate |
| PARATHION | *O*,*O*-diethyl *O*-(*p*-nitrophenyl) phosphorothioate |
| PERMETHRIN | (3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (Specify isomeric composition). |
| PROPOXUR | *o*-isopropoxyphenyl methylcarbamate |
| PYRETHRINS | (Other designation: the insecticidal constituents of pyrethrum) |
| TEMEPHOS | *O*,*O*'-(thiodi-4,1-phenylene) bis (*O*,*O*-dimethyl phosphorothioate) |
| TERBUTRYN | 2-(*tert*-butylamino)-4-(ethylamino)-6-(methylthio)-*s*-triazine |
| TETRACHLORVINPHOS | 2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate |
| TRIFLUMURON | 2-chloro-*N*(((4-(trifluoromethoxy)-phenyl)-amino)carbonyl) benzamide (C.A 64 628-44-0) |
| TRIFLURALIN | α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyn-*p*-toluidine |

# LIST OF PARTICIPANTS

| | | |
|---|---|---|
| Zitoune, S. | ALGERIA | Institut National de la Protection des Vegetaux<br>12 Avenue Pasteur<br>BP 80<br>El-Harrach |
| Ellis, K.J. | AUSTRALIA | Commonwealth Scientific and Industrial Research Organisation<br>Division of Animal Production<br>Private Mail Bag<br>Armidale N.S.W. 2350 |
| Scheffenegger, R. | AUSTRIA | Bundesministerium f. Gesundheit & Umweltschutz<br>Stubenring 1<br>A-1010 Vienna |
| Dreze, Ph. C. | BELGIUM | Faculté des Sciences Agronomiques<br>Laboratoire Central du CAMIRA<br>8 Avenue de la Faculté<br>B-5800 Gembloux |
| Schiffers, M. | | Faculté des Sciences Agronomiques de l'Etat à Gembloux<br>Passage des Déportés 2<br>B-5800 Gembloux |
| Ferreira, J.R. | BRAZIL | Centro de Energia Nuclear na Agricultura<br>Av. Centenário, S/N -C. Postal 96<br>13.400 Piracicaba - SP |
| Chen Zi-Yuan | CHINA | Institute of Nuclear Agricultural Science<br>Zhejiang Agricultural University<br>Hangzhou, Zhejiang |
| Wakid, A.F.Mehagid | EGYPT | Radiobiology Department<br>Nuclear Research Centre<br>Atomic Energy Authority<br>P.O. Box,<br>Cairo |

| | | |
|---|---|---|
| Parg, A.J. | FRG | BASF Ludwigshafen<br>Karl Boschstrasse<br>D-6700 Ludwigshafen |
| Pfister, G. | | Gesellschaft für Strahlen-und Umweltforschung mbH<br>Institut für Okologische Chemie<br>Ingolstädter Landstrasse 1<br>D-8042 Neuherberg |
| Das, K.G. | INDIA | Regional Research Laboratory<br>Hyderabad 500 009 |
| Patel, M.N. | | Microbiology and Cell Biology Laboratory<br>Indian Institute of Science<br>Bangalore 560 012 |
| Sumatra, Made | INDONESIA | Centre for the Application of Isotopes and Radiation<br>National Atomic Energy Agency<br>Jl. Cinere Pasar Jumat Kotak Pos 2<br>Kebayoran Lama<br>Jakarta Selata |
| Al-Badry, M.S. | IRAQ | Agriculture and Biology Faculty<br>Nuclear Research Centre<br>P.O. Box 765<br>Baghdad |
| Mualem, Y. | ISRAEL | The Seagram Center for Soil and Water Sciences<br>The Faculty of Agriculture<br>The Hebrew University of Jerusalem<br>P.O. Box 12<br>Rehovot 76100 |
| Imbroglini, G. | ITALY | Istituto Sperimentale per la Patologia Vegetale<br>Via C.G. Bertero 22<br>I-00156 Roma |
| Radogna, V.M. | | Istituto di Chimica Agraria<br>Universitá di Bari<br>Via Amendola 165/A<br>I-70126 Bari |
| Nazer, I.K. | JORDAN | University of Jordan<br>Faculty of Agriculture<br>Plant Protection Department<br>Amman |

| | | |
|---|---|---|
| Kawar, Nasri S. | LEBANON | c/o The Pennsylvania State University<br>Department of Entomology<br>Pesticide Research Laboratory and Graduate Study Center<br>University Park, PA 16802 |
| Minks, A.K. | NETHERLANDS | Research Institute for Plant Protection<br>P.O. Box 9600<br>NL-6700 Wageningen |
| Atu, E.G. | NIGERIA | National Root Crop Research Institute<br>PMB 7006<br>Umuahia |
| Ramon, F.V, | PANAMA | Facultad de Ciencias Nat. y Exactas<br>Universidad de Panama<br>Escuela de Quimica<br>Panama |
| Baloch, U.K. | PAKISTAN | Pakistan Agricultural Research Council<br>P.O. Box 1031<br>Islamabad |
| Czaplicki, E. | POLAND | Institute for Plant Protection<br>Miczurina 20<br>60-318 Poznan |
| Dec, J. | | Institute for Plant Protection<br>Miczurina 20<br>60-318 Poznan |
| Kurdi, A.A. Al | SAUDI ARABIA | Ministry of Agriculture and Water<br>Riyadh |
| Abiola, F.Z. | SENEGAL | Ecole Inter-Etats des Sciences et Medicine Veterinaires de Dakar<br>Boite Postale 5077<br>Dakar |
| Saidi, J.A. | TANZANIA | Agricultural Entomology Section<br>Tropical Pesticides Research Institute<br>P.O. Box 3024<br>Arusha |

| | | |
|---|---|---|
| Prabuddham, P. | THAILAND | Department of Soil Science<br>Faculty of Agriculture<br>Kasetsart University<br>Bangkhen, Bangkok 10900 |
| Tayaputch, N. | | Division of Agricultural Toxic Substances<br>Department of Agriculture<br>Bangkok 10900 |
| Adipala Ekwamu, A.E. | UGANDA | Department of Crop Science<br>Makerere University<br>P.O. Box 7062<br>Kampala |
| Astvatsatrian, B. | USSR | Armenian Research Institute of Agriculture<br>Yerevan |
| Suett, D.L. | UNITED KINGDOM | National Vegetable Research Station<br>Wellesbourne, Warwick |
| Wilkins, R.M. | | The University of Newcastle upon Tyne<br>Department of Agricultural Biology<br>Newcastle upon Tyne NE1 7RU |
| Barzin, R. | USA | Recon Associates, Inc.<br>Huguenot, NY 12746 |
| Carlson, D.A. | | USDA, ARS<br>Insect Affecting Men and Animals Research Laboratory<br>1600 SW 23rd Drive<br>P.O. Box 14565<br>Gainesville, Florida 32604 |
| Harris, F.W. | | Department of Chemistry<br>Wright State University<br>Dayton, Ohio 45431 |
| Jaffe, H. | | Livestock Insects Laboratory<br>Agricultural Environmental Quality Institute<br>BARC-East<br>USDA, ARS<br>Beltsville, Maryland 20705 |
| Knapp, F. | | Department of Entomology<br>University of Kentucky<br>Lexington, Kentucky 40546-0091 |

| | | |
|---|---|---|
| Leonhardt, B.A. | | Organic Chemical Synthesis Laboratory<br>Agricultural Environmental Quality Institute<br>BARC-West<br>USDA, ARS<br>Beltsville, Maryland 20705 |
| Scher, H.B. | | Stauffer Chemical Company<br>1200 S. 47th St.<br>Richmond, CA 94804 |
| Smith, K.L. | | Controlled Release Division<br>Bend Research, Inc,<br>64550 Research Road<br>Bend, Oregon 97701-8599 |
| Ha Minh Trung | VIET NAM | Research Institute for Plant Protection<br>Chem. Tu Liem<br>Vien Baove Thuc Vat<br>Hanoi |

## ORGANIZATIONS

| | | |
|---|---|---|
| Henriet, J. | FAO | Station de Phytopharmacie<br>Ministry of Agriculture<br>11 rue du Bordia<br>B-5800 Gembloux |
| Hassan, A. | IAEA | P.O. Box 100<br>A-1400 Vienna |
| Behechti, A.<br>Ghods-Esphahani, A.<br>Kundu, B.R.<br>Maeda, D.<br>Pascucci, C.<br>Perschke, H.<br>Vollner, 1. | | Seibersdorf Laboratory<br>A-2444 Seibersdorf |

| | | |
|---|---|---|
| Raman, K.V. | I.P.C. | International Potato Center<br>Apartado 5969<br>Lima, Peru<br>Mailing Address:<br>Department of Entomology<br>University of Minnesota<br>219 Hodson Hall<br>1980 Folwell Avenue<br>St. Paul, Minnesota 55108 |
| Medina, R. | I.F.D.C. | International Fertilizer Development Center<br>Muscle Shoals, Alabama |

# HOW TO ORDER IAEA PUBLICATIONS

**An exclusive sales agent for IAEA publications, to whom all orders and inquiries should be addressed, has been appointed in the following country:**

| | |
|---|---|
| UNITED STATES OF AMERICA | UNIPUB – Bernan Associates, 10033-F King Highway, Lanham, MD 20706-4391 |

---

**In the following countries IAEA publications may be purchased from the sales agents or booksellers listed or through your major local booksellers. Payment can be made in local currency or with UNESCO coupons.**

| | |
|---|---|
| ARGENTINA | Comisión Nacional de Energía Atomica, Avenida del Libertador 8250,<br>RA-1429 Buenos Aires |
| AUSTRALIA | Hunter Publications, 58 A Gipps Street, Collingwood, Victoria 3066 |
| BELGIUM | Service Courrier UNESCO, 202, Avenue du Roi, B-1060 Brussels |
| CHILE | Comisión Chilena de Energía Nuclear, Venta de Publicaciones,<br>Amunategui 95, Casilla 188-D, Santiago |
| CHINA | IAEA Publications in Chinese<br>China Nuclear Energy Industry Corporation, Translation Section,<br>P.O. Box 2103, Beijing<br>IAEA Publications other than in Chinese<br>China National Publications Import & Export Corporation,<br>Deutsche Abteilung, P.O. Box 88, Beijing |
| CZECHOSLOVAKIA | S.N T L., Mikulandska 4, CS-116 86 Prague 1<br>Alfa, Publishers, Hurbanovo námestie 3, CS-815 89 Bratislava |
| FRANCE | Office International de Documentation et Librairie, 48, rue Gay-Lussac,<br>F-75240 Paris Cedex 05 |
| HUNGARY | Kultura, Hungarian Foreign Trading Company,<br>P.O. Box 149, H-1389 Budapest 62 |
| INDIA | Oxford Book and Stationery Co., 17, Park Street, Calcutta-700 016<br>Oxford Book and Stationery Co., Scindia House, New Delhi-110 001 |
| ISRAEL | Heiliger and Co., Ltd, Scientific and Medical Books,<br>3, Nathan Strauss Street, Jerusalem 94227 |
| ITALY | Libreria Scientifica, Dott. Lucio de Biasio "aeiou",<br>Via Meravigli 16, I-20123 Milan |
| JAPAN | Maruzen Company, Ltd, P.O. Box 5050, 100-31 Tokyo International |
| PAKISTAN | Mirza Book Agency, 65, Shahrah Quaid-e-Azam, P O. Box 729, Lahore 3 |
| POLAND | Ars Polona-Ruch, Centrala Handlu Zagranicznego,<br>Krakowskie Przedmiescie 7, PL-00-068 Warsaw |
| ROMANIA | Ilexim, P O. Box 136-137, Bucharest |
| SOUTH AFRICA | Van Schaik Bookstore (Pty) Ltd, P O. Box 724, Pretoria 0001 |
| SPAIN | Díaz de Santos, Lagasca 95, E-28006 Madrid<br>Díaz de Santos, Balmes 417, E-08022 Barcelona |
| SWEDEN | AB Fritzes Kungl. Hovbokhandel, Fredsgatan 2, P.O. Box 16356,<br>S-103 27 Stockholm |
| UNITED KINGDOM | Her Majesty's Stationery Office, Publications Centre, Agency Section,<br>51 Nine Elms Lane, London SW8 5DR |
| USSR | Mezhdunarodnaya Kniga, Smolenskaya-Sennaya 32-34, Moscow G-200 |
| YUGOSLAVIA | Jugoslovenska Knjiga, Terazije 27, P.O Box 36, YU-11001 Belgrade |

---

**Orders from countries where sales agents have not yet been appointed and requests for information should be addressed directly to:**

**Division of Publications**
**International Atomic Energy Agency**
**Wagramerstrasse 5, P.O. Box 100, A-1400 Vienna, Austria**