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PESTICIDES DEVELOPMENT PROGRAMME IN INDIA

DP/IND/80/037

INDIA

Technical report: Preparatory assistance for the establishment of biological testing ~~facilities~~*

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Clive E. Price
Expert in biological evaluation of ~~pesticide~~ formulations

United Nations Industrial Development Organization
Vienna

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I wish to thank the PDPI and HIL staff at Gurgaon for their hospitality and co-operation during the period of this mission, with a particular word of thanks to Dr. S. K. Khetan for his support and encouragement. Most of the period of this mission was shared with Dr. Wade Van Valkenburg, whom I thank for the many fruitful hours we spent discussing the future development of PDPI. I would also like to express my appreciation of the support given to me by Dr. M. K. Hussein and Mr. S. Pal of UNDP.

INTRODUCTION

The Pesticides Development Programme in India was set up in 1981 with the following objectives:

1. (a) To assist the Government in surveying the pesticides demand and supply situation in the country so that gaps between demand and supply can be detected at an early date and high cost emergency acquisition of pesticides eliminated or kept at minimum.

   (b) To identify, assess and test local raw materials and fillers for formulation.

   (c) To recommend the most suitable pesticides.

2. Planning, co-ordination and promotion of the pesticides industry in the country.

3. Expansion and modernisation of the existing units as well as planning of new units.

4. Feasibility of setting up new plants, the required infrastructure and investment, proper distribution and marketing of products.

5. Evaluation of proposals to set up pesticides production or formulation plant.

6. Develop formulations specifically suitable for local production and use in the various states.

7. Adaptation of imported technology, both in the production and formulation of pesticides, to best suit conditions of the regions concerned.

8. Assessment of equipment suppliers.

9. Prepare proposals for the standardization and quality control at plant or supplier level.

10. Set up an information and documentation service and disseminate information on technology and market.

11. Manpower and technical skill development by organizing training course/ seminars in the following specific areas:

    i) Production of various types of pesticides;

    ii) Formulation of pesticides;

    iii) Quality control.

iv) Plant maintenance;

v) Packaging;

vi) Marketing and distribution;

vii) Protection of the environment from the use of pesticides and monitoring harmful effects and residues.

viii) Application of pesticides.

12. Assist the Government and Industry in organizing regional Government Consultations on a coordinated sectoral development effort.

13. Assist in developing basic data under the Insecticides Act for the registration of products with the Insecticides Board.

14. Advise and assist the industry in any of the related issues, especially toxicity, pollution control and other allied matters, so that pollution control efforts could be effectively coordinated.

Progress during the first two years was behind schedule and so a less ambitious programme was agreed with the following objectives:

1. To develop new formulations and improve existing formulations specifically suitable for local production and use.

2. To identify, assess, test and propose detailed specifications of various raw materials such as fillers, solvents and surface active agents available in the country for the production of formulations.

3. Standardization of quality control and safety methods for the fomulation industry.

4. Development of trained manpower for the industry, particularly with reference to the small scale sector.

5. Setting up as a part of the institution, a strong documentation centre with library and seminar facilities, including creating a data bank on various aspects of pesticide manufacture.

PDPI occupies part of the Central Research and Development complex of Hindustan Insecticides Limited (HIL) at Gurgaon in Haryana, 25 km south of Delhi. There are three main buildings, a combined laboratory and administration building, a laboratory block and a pilot plant building. All three buildings are shared between PDPI and the HIL Divisions of Administration, Biological Science and Pesticide Synthesis and Process Development. There is also a small library in the laboratory block, a separate boiler room for generating steam, and a small greenhouse. The buildings are set in about 70 acres of land, of which 40-50 acres are earmarked for an experimental farm.

The Biological Science Division consists of two entomologists with a small team of laboratory and field workers. They were previously working under the direction of the PDPI research manager but now report directly to HIL.

The period of the consultancy was two months, from 28 February to 25 April 1986, and my responsibilities, as stated in the conditions of employment, were as follows:

The consultant is expected to advise and assist scientists of the Pesticide Development Programme India (PDPI) on:

- Propagating weeds and crops of the region in glass houses for screening;
- Screening of formulations developed in PDPI, on the type of formulations that could be tested at exploratory level, including pesticide mixtures for both pre- and post-emergency activity;
- Use of standards for comparison;
- Application methods for constant dosages, repeatability and reproducibility of results;
- Proper documentation of the results for logical comparison.

In addition, the expert is expected to give lectures to the scientists of PDPI on various aspects of herbicide screening, methodology, mode of action and different application methods to suit local conditions. He is expected to submit a report to UNIDO on his findings and recommendations.

For the purposes of this consultancy I defined PDPI as the entire Gurgaon complex because there were no biologists officially attached to PDPI. The objectives were not fully attained because there were no suitable greenhouse facilities or equipment. A start was made on propogating weeds and crop plants but no formulations were tested. A number of lectures were given.

II.THE NEED FOR BIOLOGICAL TESTING.

A. Background.

The emphasis at PDPI in the past has been on a technical base for producing formulations. Previous experts have been concerned with formulation technology analysis and the use of scientific equipment. The PDPI staff are long-term HIL employees and so their main experience has been with contact insecticides such as DDT where biological activity is usually considered to be more closely related to the physical properties of the formulation. Consequently, there was a need to:

a) demonstrate that formulations had a significant effect on biological activity.

b) explain the complexities of the biological system and why it is difficult to predict the effect of formulation changes on activity.

c) present the state-of-the-art formulation effects on biological activity.

d) show how climatic conditions influence the performance of a formulation and relate this data to the Indian conditions.

B. Lectures.

The relevance of biological testing to formulation development was presented in a series of lectures. The first lecture was to senior executives from the pesticide formulation industry who were attending a three day concept meeting organised by PDPI (Annex.1). The main aim of this lecture was to show that formulations could be designed specifically for particular climatic regions, and that formulators had an important part to play in this context. A similar lecture was given at the Frederick Institute of Plant Protection and Toxicology near Madras (Annex 5).

A subsequent lecture was given to PDPI staff on pesticide screening methods with emphasis on the technical details of the methods and the importance of good communications between the biologists and the formulation chemists (Annex 2). This lecture also dealt briefly with different methods of application, including the use of very low volume equipment. These lectures were directed primarily at the chemists who needed to be convinced that biological testing was necessary. The biologists were already convinced of the need but will benefit from further practical training when the facilities are available.

The role of formulation adjuvants on pesticide activity was a recurring theme during discussions at PDPI and formed part of my lectures at the concept meeting, subsequently expanded to a lecture to the PDPI staff (Annex 3). Some of the more theoretical aspects were expanded in a lecture given at Anna University, Madras in their series "Horizons in Biotechnology" (Annex 6). At the moment PDPI are concentrating on getting the new technology to work, so it is unlikely that they will move into these more complex areas until they have a specific problem that requires it. A joint lecture on the effect of chemical structure on formulations was given with Dr. Van Valkenburg, and this included some discussion on the role of different formulations on the salt and ester forms of the same pesticide (e.g. 2,4-D). (Annex 4).

III. NEW PROJECTS

A. Formulation and Testing of Biocides

Professor Kunthala Jayaraman of A. C. College of Technology, Madras, requires assistance to formulate a protein complex from Bacillus sphaericus, and has made initial contact with PDPI with a view to contracting them to undertake the work. The formulation of polypeptides is extremely difficult and is further complicated in this case by additional physical properties which are needed to make the active ingredient available to the target organism, mosquito larvae. Technically this is a very difficult problem and it should not be considered until some provision is made, either to accommodate one of Professor Jayraman's staff at PDPI to carry our the biological testing or to appoint a biologist to the PDPI staff. The formulation of biological materials requires a very high input from biochemically trained scienctists and can only be undertaken successfully if PDPI are in a position to utilise all the expertise available to them. If they are to undertake this type of work in the future, they should employ a physiologist/biochemist who can maintain close relations with laboratories involved with natural products.

B. Basalin Formulation

BASF India have contracted PDPI to reformulate their herbicide basalin. This herbicide is applied to the soil surface before the rains start when it is washed into the soild and prevents weed seed germination. The chemical is lost during the pre-rain period by volatilization and photodegradation. Work has only just started on this project but there are no plans to test the formulations for their biological activity at PDPI.

In conclusion both these projects would present considerable technical difficulties and further strenghening of PDPI with qualified and trained technical staff with specific responsibilities for individual research projects is essential.

3. SETTING UP A BIOLOGICAL TESTING UNIT

If PDPI is to test pesticide formulations for their biological activity they will need a major investment in facilities and manpower. The three main types of pesticide, fungicide, insecticide and herbicide, will each need a specialist biologist with one of them, preferably the herbicide specialist, taking responsibility for growing all test species. Support staff will be needed for laboratory and greenhouse work. The technical or organisational requirements of these support staff require that each of the three areas of responsibility and the plant growing unit should have a graduate assistant.

A. Greenhouses.

Four greenhouses will be needed, one for each type of pesticide and a larger one for growing test plants. The greenhouses for insecticides and fungicides should be compartmentalised to prevent the spread of test organisms. Greenhouses were visited at the Quarantine Department of Public Health, Delhi and at ICRISAT (Hyderabad). Further enquiries will be undertaken upon my return to the UK. Discussions at these two greenhouse sites included shading and methods of cooling and I am informed that unshaded greenhouses at ICRISAT require one Braemar cooler for every 400 square feet of floor space. The Australian quarantine greenhouses near Delhi were shaded to reduce internal temperatures but the light intensity was also much reduced. At Gurgaon, Dr. Ramdev took measurements of temperature, humidity and PAL light intensity (photosynthesis active light) in the greenhouse compartments and outside in full sun and in the shade using instruments I brought with me from the UK. The measurements were taken at hourly intervals on a cloudy day and a sunny day and revealed very large variations in different parts of the greenhouse caused by poor design.

B. Growth rooms

Stocks of insects and pathogens will need to be maintained at the Gurgaon site for infecting plants prior to spraying with pesticides. These rooms will need accurate temperature and humidity control and a reliable electrical supply 24 hours per day. Currently, insects are reared in a laboratory and there is no power on the site from 5 pm to 9 am. A smaller controlled environment room is needed to stock weed and crop seeds. A shelter for preparing soil, filling pots, seeding etc. will also be required.

C. Plant propogation.

Seeds were collected from Argemone Mexicana, Tribulus terrestris and Asphodelus tenuifolius plants growing at the PDPI station. Further seeds will be collected by the biologists in preparation for future herbicide trials. It is significant that, as far as I know, none of these weeds are included in the herbicide screens of any multinational agrochemical company. Perennial weeds are far more difficult to control than annual weeds because effective control requires a detailed understanding of their physiology and morphology, Cyperus rotundus plants were dug up to show the relationship between the rhizome and the underground tubers (swollen nodes), and to demonstrate the depth at which they can occur in dry soil. Cynodon dactylon was also collected as a contrast to Cyperus because in this species any node on the rhizome is potentially viable. The rhizome was cut into one, two and three node lengths and planted in pots, other pieces of rhizome were planted in soil. At the end of four weeks the two and three node pieces were growing well and the one node pieces were either sprouting or were well established. However, the rhizome planted in pots grew less rapidly than those in the same soil in open ground, and 20 Citrus seeds sown in pots produced only a single plant. Work will need to be done to improve the potting characteristics of the Gurgaon soil and a sample of crushed rock phosphate was obtained from Project DP/IND/81/019 (Investigations to use low-grade phosphate from Mussoorie deposit) to assess its value as a compost additive. Lack of suitable working conditions prevented detailed work on development of a potting soil, but this must be a first priority when a greenhouse and potting shelter are available. There will also be a need for plastic plant pots as the available earthenware pots retain too many pesticide residues and are too variable in their shape, size and physical properties.

D. Spray equipment and minor items.

Formulations should be designed to take advantage of the equipment that will be used for application. For example, drift spraying using spinning disc applicators performs best with non-drying formulations because the small droplets have such a high surface area to volume ratio. A wide range of spray equipment is essential so that trials can relate to all possible farmer application methods. Equipment should include conventional pressure and knapsack sprayers with a good range of jets including very low volume jets such as the Cooper Pegler VLV series and a selection of Micron controlled droplet applicators (CDA) using spinning disk technology. CDA applicaters are becoming increasingly important in many tropical and sub-tropical regions because they require less water and enable workers to treat much larger areas within the same time scale. A track sprayer is the most expensive item but is essential for the accurate application of lage numbers of formulations to plants growing in pots. A Mardrive pressure driven system is one of the best available and requires very little maintenance.

There are many other small items of equipment required for trials work that are not available at the PDPI site at Gurgaon, such as a small cultivator and a range of hand tools. At the moment trial plots are largely prepared by hand but this is not a safe practice if the soil has been treated with pesticides and is far too slow for large scale trials. Simple soil sterilising equipment will be required (the existing steam generater could be used for this purpose), together with a large volume soil mixer for preparing potting compost.

All trials data should be computerised from the very beginning and the selected hardware and software should be capable of future expansion to avoid later changes and re-input. Simple temperature and humidity recording equipment should be installed in all the greenhouses as part of the quality control procedure, and more accurate measuring equipment, including light intensity, should be available for experimental purposes.

E. Library facilities.

The library accommodation is adequate but the range of books and journals is not. Indian journals are conspicuous by their absence but are essential reading for information on national pest problems. Recommended additions are:

Indian Journal of Entomology

Indian Journal of Weed Science

Indian Journal of Phytopathology

Indian Journal of Soil Science

Indian Journal of Agricultural Science

Indian Farming

More reference books are also required, especially for the biologists. The library should be air conditioned and available to staff throughout the normal working day.

F. Relations with other Institutes.

There are no strong contacts between PDPI and other organizations involved with pesticides. This will become important when PDPI enters the field of biological testing because they have no long term experience in this area. The most obvious local institute is the Indian Agricultural Research Institute which is already running field trials on formulations in a highly professional manner. They are also involved in pesticide formulation and have expressed an interest in attending PDPI lectures. Closer liason with this and other institutes of the Indian Council of

Agricultural Research is essential if PDPI wishes to occupy a leading position in the pesticide industry. It should also be closely involved with the All India Co-ordinated Projected programmes.

Contacts with other institutes should include centres representative of different climatic regions so that local trials can be organised more conveniently and local problems brought to PDPI's attention. Institutes concerned with specific crops are important as possible testing agencies for new products and for highlighting potential problems before they become epidemics, and contact with ICRISAT at Hyderabad could lead to international contracts, especially in India. If the formulation of natural products is to be a recurring feature of PDPI activities then closer relations with the Regional Research Laboratory, Hyderabad would be an advantage.

Many of the problems inherant in the Gurgaon site, such as unsuitable climate for fungal diseases and many insect pests, could be minimised by liason with a south Indian research station. The Frederick Institute would in many ways be an ideal candidate for this because they have very strong biological and toxicological sections but a very weak formulation section, the exact opposite to PDPI. They have already established a reputation with the pesticide industry and have set up formal relations with the University of Madras help them establish a strong research team.

G. Manpower.

PDPI is undermanned. There are currently only 14 of the proposed 35 planned staff on the project, covering every aspect of formulation from research into new types of formulations to pilot plant production. Analysis of clay materials is taking one team which will diversify into colloid science later this year. With only one formulation team it is not even possible to work on two problems at the same time. This means that there is little potential for producing enough formulations to keep three biological teams busy, and yet it is not feasible to try to combine any two of the three pest discipline because the training is so complex. Any compromise on this point will lead to inefficiency or a strong possibility of generating unreliable data. The alternative is to form a working alliance with an institute, such as the Frederick Institute in Madras, which has a strong biological group but a very weak formulation team. This may not be ideal from the formulation chemists point of view but it may be the only possible way of obtaining biological data. I can see that the only way Professor Jayaraman will get her biocide formulations tested will be to have them sent to her own laboratory in Madras.

The main problem in having the biological testing carried out off site, is that there will be a tendency for the chemists to revert to not testing formulations for biological effectiveness. It

must be stressed that PDPI are operating with totally inadequate manpower levels in relation to the breadth of their responsibilities.

4. FUTURE DEVELOPMENT

A. The position of PDPI in the Indian agrochemical environment.

There is some confusion regarding the role of PDPI and the way it can achieve its objectives. The original objectives made PDPI in many ways a government advisory service with research and teaching responsibilities. When the objectives were re-drawn three important objectives were omitted:

1 (a). To assist Government in surveying the pesticides demand and supply situation in the country so that gaps between demand and supply could be detected at an early stage and high cost emergency acquisition of pesticides eliminated or kept at a minimum.

1 (c). To recommend the most suitable pesticides.

2. Planning, coordination and promotion of the pesticides industry in the country.

This left PDPI with responsibility for developing formulation expertise and for training the agrochemical industry in formulation techniques. Training and research are the traditional roles of research institutes and universities, who are financed for that purpose, but PDPI are now developing a strategy which should provide a valuble service for the Indian agrochemical industry:

1. Training courses have been organised and will continue.

2. Intensive 'in house' training will be developed when facilities are available.

3. Contract research on specific problems will be undertaken for individual companies. This will include formulating pesticides and the analysis of formulation raw materials.

This increased commercialisation of the services offered by PDPI will require changes in its management structure:

1. It will need to give a confidential service to customers and therefore must be partially independent of HIL.

2. Financial independence is essential for its day-to-day running expences.

3. Its research potential will need to be strengthened.

B. Operational independence

This is essential from the point of view of PDPI and more especially its customers. HIL is perceived as a competitor of the companies who will be bringing research projects to PDPI. They will need to be assured that the research results, or even details of the research proposal, will not be made available to HIL. At the moment payments for PDPI training courses are made to HIL, which gives the impression that PDPI is only the research department of HIL, and that confidentiality is not possible. PDPI management also need to make their own decisions within the guidelines set up by their governing body but without having to obtain approval from HIL. For this they need some degree of financial independence.

C. Financial structure

With the loss of the three objectives originally proposed by the Indian Government, PDPI lost its role as adviser to the Government and was relegated to providing a service for the agrochemical industry only. Under these circumstances it is unrealistic to expect full Government support for all future activities. HIL also cannot be expected to finance PDPI activities which are intended to improve the formulating skills and efficiency of its competitors. It is clear that alternative funding is essential to give PDPI some level of independence from HIL and to assist its long term development. The current proposal is to charge customers for services rendered, but this can lead to problems which in the long term will reduce PDPI's contribution to the development of the Indian agrochemical industry. The major problem is that any organisation that undertakes contract research must give priority to the financial return. High paying contracts will receive priority, irrespective of technical or scientific merit. Inevitably, any organisation servicing the individual components of an industry will lose its leadership role. It will also become apparent that advanced training will lose PDPI its research customers because they will then be able to carry out the research themselves. Under these circumstances training may well be seen to be the responsibility of universities.

If PDPI is to play a full role in the long term development of the Indian pesticide industry it should be funded centrally and given the clear remit of serving the industry as a whole. In the short term it may have to undertake contract research in order to prove its value to the industry.

D. Research development

In order to continue to develop as a centre of excellence after UNDP support ends, PDPI must establish a strong research momentum and for this a small group of Post Graduate research students is essential. It should be possible for PDPI to achieve this by affiliating with a suitable university (the Frederick Institute has affiliated with the University of Madras).

The location of the Gurgaon site means that transport is essential so that students can get to the library facilities at their educational base (the affiliated institute). The site services will also need to be improved as students frequently need to keep some experiments running overnight.

V. CONCLUSIONS

There are important decisions to be made on the future development of PDPI, in particular, what is expected of PDPI? It is well set up to carry out contract research for agrochemical companies and to give basic training courses in formulation technology but this will not necessarily provide it with the resources or incentive to lead the Indian agrochemical industry to greater technical achievements. To do this effectively, some form of central funding from Government or the Indian Agrochemical Association is essential.

VI. RECOMMENDATIONS

1. Careful consideration should be given to the implications of biological testing within PDPI, with particular reference to the long-term manpower requirements. Collaboration with other institutes such as the Indian Agricultural Research Institute or the Frederick Institute may be more cost effective.

2. Consideration should be given to the detailed long-term development of PDPI including a formal liaison with other institutes or centres of post-graduate training.

3. If PDPI is to obtain contracts from other pesticide companies, it must be seen to be an independent setup. It is clearly not possible for PDPI to achieve complete independence without major changes in management structure, manpower and legal status which are unlikely to be achieved within the period of the two year extension.

4. Detailed discussions should be held in New Delhi during the next year on the long-term role of PDPI with particular reference to how it will be funded and how its technical expertise can be most effectively applied to the development of the Indian Agrochemical Industry.

5. If it is agreed that PDPI should set set up its own biological testing facilities, the following equipment will be required:

3 Greenhouses with benches and coolers etc.

1 Mardrive track sprayer

3 Birkmier stainless steel pressure sprayers

5 Cooper-Pegler knapsack sprayers with accessories and jets including the VLV range

5 Micron herbi CDA applicators

5 Micron Ulva CDA applicators

10,000 Plastic pots, various sizes

500 Plastic trays

1 Top pan balance

1 Soil mixer

1 large capacity scales

Biological books and journals

1 Ferranti PC AT computer

1 Skye instruments PAL meter

1 Kane-May 8004 temperature and humidity meter

4 Casella temerature and humidity recorders

ANNEX 1

BIOLOGICAL ACTIVITY AND FORMULATION CHEMISTRY.

To the farmer, a pesticide is not a chemical, it is a biological effect. The role of the formulation is to ensure that the optimum biological effect is available to the farmer in a way that is safe, convenient and cost effective. All too often, however, the emphasis on formulation design is on physicial and chemical stability and convenience, with relatively little attention given to optimising the biological activity.

Getting the pesticide onto the leaf or soil surface may be all that is required of an insecticide or a fungicide, subsequent action being determined by the arrival of an insect eating or walking over the leaf or fungal spores germinating on it, but the formulation may also improve the biological effect by assisting the active ingredient to penetrate into the target organism or may enable the pesticide to accumulate in plant tissues where it is more accessible to the organism. Penetration into the plant is clearly essential for pests and diseases which occupy internal tissues, but it is also important for leaf surface insects, such as aphids, feeding on internal tissues (phloem), or fungal pathogens, such as powdery mildew, sending haustoria into epidermal cells. Any herbicide or plant growth regulator must penetrate at least as far as the photosynthetic tissues if it is to have any effect, and this is true also of systemic insecticides and fungicides which rely on translocation in the plant for their full effect (Fig.1).

Each stage in the process from formulation to accumulation at the site of action is dependent on what happens at the preceeding stages, for example, a poor formulation may precipitate when diluted for spraying and therefore will not arrive at the leaf or soil surface in a suitable form. Similarly, if uptake into the plant is poor then there is less chemical available for translocation.

To what extent can formulation adjuvants improve the activity of a pesticide ? There are numerous cases described in the literature showing that formulation adjuvants can more than double the apparent activity of pesticides, but the specific way in which this is accomplished is seldom apparent. Surfactants, for example, were originally added to formulations to assist retention of spray deposits by leaves, but there is now a considerable amount of data showing that they also improve uptake (Table 1).

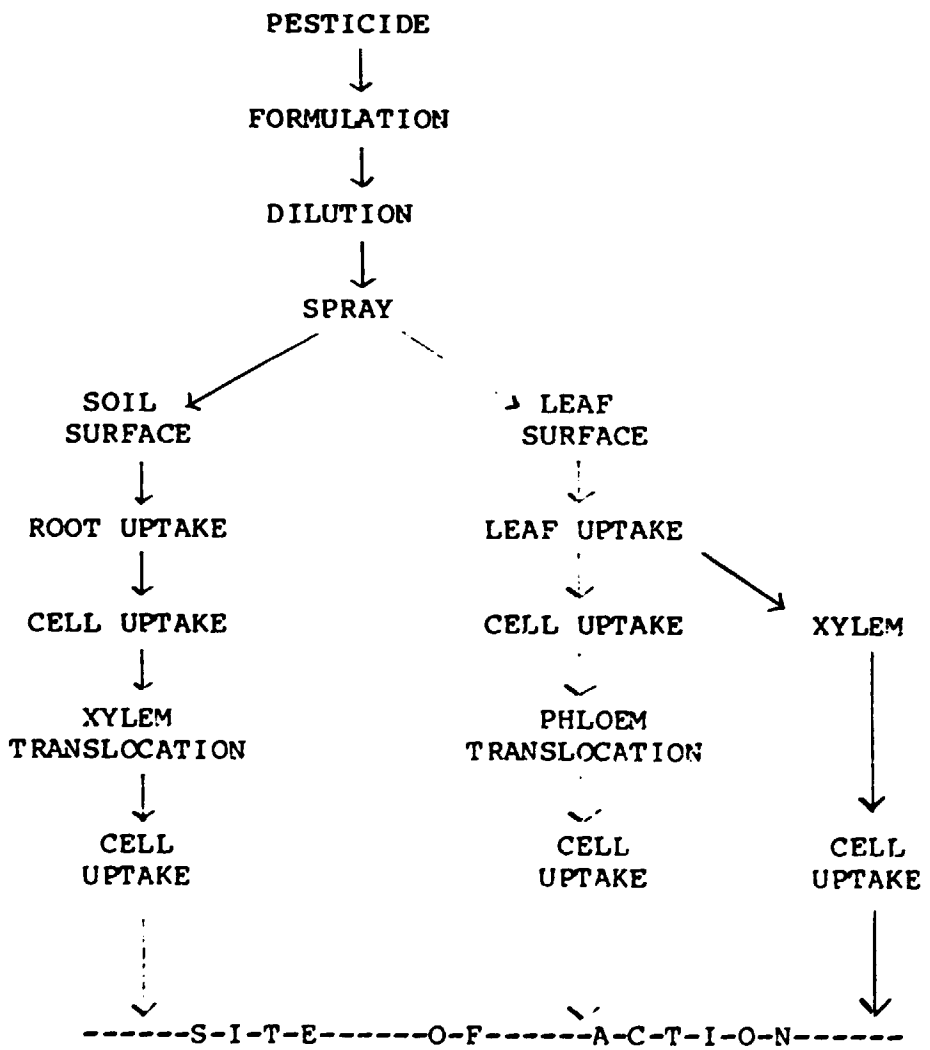
TABLE 1

THE UPTAKE OF GIBBERELLIC ACID INTO GREEN NAVEL ORANGES

Standard formulation (no surfactant)	12%
0.1% surfactant formulation	68%

FIGURE 1

THE PATHWAYS OF PESTICIDE UPTAKE



The way in which surfactants assist uptake is not fully understood but it is probable that both surfactants and solvents influence penetration by modifying the physical properties of the pesticide deposits on the leaf surface and the permeability of the cuticle itself.

It is generally accepted that compounds cross the cuticle by diffusion. The rate of diffusion is inversely proportional to molecular radius, which means that large molecules or molecular agregates are not able to cross the cuticle in significant quantities. Under some circumstances surfactants increase uptake by retaining water in the spray deposit and preventing it from drying out. When this happens a high concentration of solute is maintained in the deposit and uptake is prolonged, possibly for a period of days. It has also been shown that pesticides applied as solution-particulate mixtures can penetrate the cuticle in quantities greater than the dissolved part alone. The explanation for this is that the solid phase of the active ingredient continues to dissolve after the solubilised fraction has penetrated, increasing the quantity of pesticide available for uptake. For example, the uptake of ethirimol from a suspension concentrate was three times greater than from a saturated solution and continued for several days after uptake from the solution had stopped, clear evidence that ethirimol in the solid state had entered solution and contributed to the total uptake. This aspect of pesticide uptake can be manipulated by careful selection of formulation adjuvants. For instance, the inclusion of an humectant or an high HLB surfactant will help the retention of water so that sufficient mobile phase is available for solid particles of a pesticide to continue to enter solution and diffuse into the cuticle.

The transport of solutes across the cuticle is at least partly determined by the physical properties of the solute, but the relationship between partition, for example, and uptake may be different for different plant species (Table 2).

TABLE 2

THE UPTAKE OF 2,4-D SALT AND ESTER

FROM THE SAME FORMULATION INTO FOUR WEED SPECIES

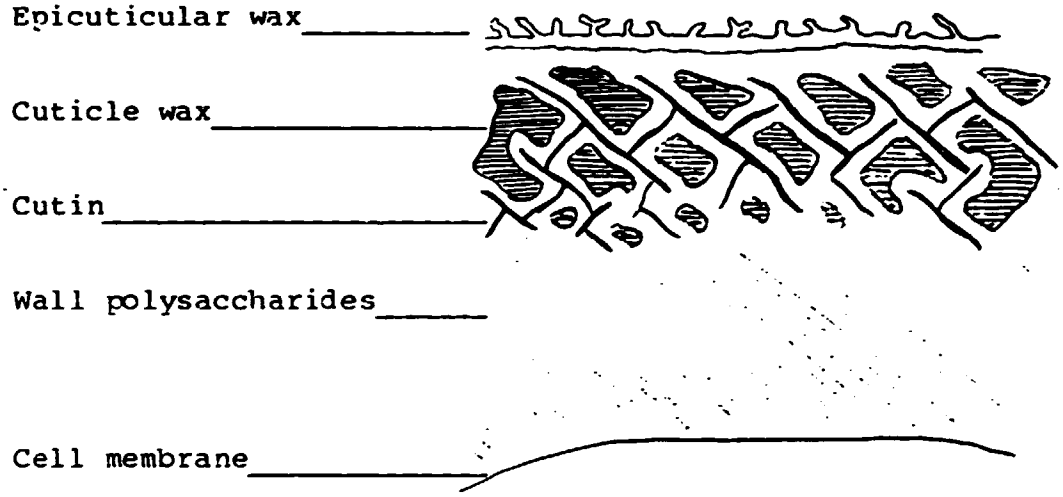
Compund	Xanthium	Amaranthus	Cyperus	Ipomoea
2,4-D SALT	81	78	34	38
2,4-D ESTER	60	78	59	60

(Figures are percentage uptake after 24h into Xanthium pennsylvanicum, Amaranthus retroflexus, Cyperus rotundus and Ipomoea leari, all growing under field conditions in Spain. The approximate Log.Partition (octanol) for 2,4-D ester is 5.7 and for the sodium salt -1.4).

The reason for the differences in uptake are not well understood but they may reflect differences in the structure and composition of the cuticle of the different species (Figure 2). The main structure of all plant cuticles consists of cutin, a three dimensional complex of cross linked hydroxy-fatty acids. Cuticular wax is embedded within the cutin, and epicuticular wax forms a layer on the surface. Hydrophylic pectins and cellulose underly and penetrate the cuticle, creating a gradient of polarity extending from the epicuticular wax on the outside, to the cuticle - wall boundary at the inside. The permeability of pesticdes with different physical properties will be controlled by the composition and relative proportions of cutin, waxes and polar components in the cuticle, but the exact nature of the interaction is not understood.

FIGURE 2

CUTICLE STRUCTURE



The cuticle-pesticide interaction is further complicated by the impact of the formulation adjuvants on the structure of the cuticle. Surfactants and solvents are known to cross the cuticle and it is probable that they dissolve, redistribute or otherwise modify the cuticle components when they do so, producing complex effects on pesticide uptake that may be species specific. The data given in Table 3 illustrates a possible case where surfactants are modifying the transport of substances across the cuticle. The response of the three species to the surfactants is quite different, which suggests that the surfactants are exerting their effect within the cuticles, which have different structures and compositions, and not within the spray deposits on the cuticle surfaces which are determined largely by the ambient environmental conditions and are therefore reasonably uniform for all the species.

TABLE 3

THE UPTAKE OF ETHIRIMOL INTO THE LEAVES OF THREE PLANT SPECIES

Surfactant	Ipomoea sp.	Cotton	Orange
SYNPERONIC A2	48	33	18
" A7	51	32	22
" A20	53	36	28
" NP8	31	15	4
AEROSOL OT	44	18	3

The full complexity of the impact of adjuvants on pesticide uptake is seen when formulations are used on the same species in different countries (Table 4). The reduced uptake of ethirimol under the hotter, dryer conditions of Australia can be explained as resulting from the more rapid and complete drying of the spray deposit. The improved uptake of permethrin may be because it is closer to its melting point and the melting point of the cuticle waxes.

TABLE 4

THE UPTAKE OF ETHIRIMOL AND PERMETHRIN INTO ORANGE LEAVES UNDER DIFFERENT CLIMATIC CONDITIONS

Compound	Spain	Australia
ETHIRIMOL	20	9
PERMETHRIN	16	32

The important conclusion from these data is that the same formulation will perform with different efficiencies in different environments, a strong argument for formulating the pesticide for the region in which it will be applied. An additional advantage of local formulation is that local pest problems can be included in formulation efficacy trials.

The costs of pesticide active ingredients are high relative to the costs of formulation adjuvants, so formulations that increase the biological activity of the active ingredient may reduce the price of the product and bring it within the reach of the farmer. There are also increasing demands that for environmental reasons the quantities of chemical spread over farming land should be limited, which again means that the aim must be to obtain the maximum biological activity from the minimum chemical. This will provide the next major challenge to formulation chemists and require careful biological assessment of formulations and greater understanding of the physico-chemical parameters which control biological effectiveness.

ANNEX 2

TESTING FOR BIOLOGICAL ACTIVITY

All formulations need to be tested for their biological activity before they are put into the market, because to the farmer, biological activity is what he is paying for when he buys the product. Physical properties such as emulsion stability, dispersibility etc are a part of biological activity because poor physical properties ultimately lead to poor biological performance but good physical properties do not necessarily mean good performance. There are very few reliable ground rules for predicting biological performance which means that biological testing must be an integral part of formulation development in order to obtain a suitble combination of physical properties and biological activity.

In biological terms, the least complicated type of pesticide to formulate are those which exert their effect on the surface of the plant. For solid fungicides such as sulphur or dichloronaphthoquinone the critical parameter is small particle size and even distribution over the surface. Similarly, the liquid pyrethroid insecticides are formulated as emulsifiable concentrates which are again intended to present a good surface cover. Parts of the leaf which are not covered may be susceptible to attack, for instance, pyrethroid insecticides sprayed by conventional equipment onto cotton, give little protection against white fly because spray droplets land mainly on the upper surface of the leaves while the insects live on the lower surface. If the same pyrethroid insecticide is sprayed by Electrodyn equipment each droplet receives an electric charge which attracts it to the leaf surface, including the lower surface, so killing the white fly.

Protecting the whole plant is a major difficulty when applying contact pesticides, whether it is covering lower surfaces of leaves, or parts of the plant covered by upperleaves or even protecting leaves which have developed subsequent to the application of pesticide. Many of these problems can be avoided by the use of more sophisticated systemic pesticides. A systemic pesticide enters the plant and moves in the tissue, possibly protecting the lower surface of leaves (translaminar activity), and usually moving with the transpiration water in the xylem in an upward direction. Chemicals such as benlate and pirimicarb are taken up through roots or the lower parts of the stem and translocated to all above ground parts of the plant.

The formulation of systemic compounds is far more difficult than contact pesticides because their biological activity depends on their ability to penetrate into plants. This is even more true of herbicides and plant growth regulators which have no activity at all on the plant surface. A formulation which doubled uptake

would double activity. Formulation adjuvants can have a big effect on the uptake of a pesticide but there is, so far, no reliable guide for the selection of the ideal adjuvant for a particular situation. It is known, however, that the selection of adjuvants for optimum uptake will depend on the plant species, the active ingredient, and the climatic conditions.

The most reliable way to select the adjuvants giving optimum activity is to prepare a relatively large number of formulations and to test each one for biological activity. The tests must be carried out rapidly so that the results can be incorporated into the next formulations. This requires a close interaction between the formulation chemists and biologists.

Biological tests fall into three broad categories:

1. Greenhouse
2. Plot
3. Field

Greenhouse Tests

Greenhouse tests are the first to be carried out and provide most of the data. The plants are grown in pots containing a uniform soil type. Climatic conditions in the greenhouse are maintained as uniform as possible and adjusted to suit the pest, disease or plant species under test. The plant pots should be non-porous and the soil modified by the addition of sand and organic material to give good aeration and drainage. Chemical application can be very uniform under these conditions either using hand sprayers or, preferably, a track sprayer.

Plot Trials

Selected formulations are taken from the greenhouse into small plots 2 x 6 m under field conditions. This has the advantage that the plants are growing more naturally and soil effects can be taken into account. Crop plants can be realistically grown to yield. The main disadvantages are seasonal and regional effects. The plants should be grown under natural conditions, if possible, and at the correct time of year. This limits the opportunity for trials especially in parts of India with marked seasonal differences in temperature. There are also problems in establishing adequate levels of pest or disease. Trials on soil applied residual herbicides are preferably tested, at this stage, under high rainfall, tropical conditions where leaching and metabolism are relatively rapid. Subsequent tests should include all proposed user conditions.

Field Trials

The final tests are those relating to farmer use where the formulation will be tested by farmers in collaboration with scientists to assess the impact of local conditions and farming practice on the effectiveness of the product.

One of the most important benefits from farmer trials is that biologists who relate to the formulation chemists actually see how the farmer uses the product on trial. Some of the problems may be local, for instance water quality can affect the product unless special modifications are made to the formulation, but close contact with farmers may also reveal emerging problems such as new pests or changes in application methods; an example of the latter is the increasing use of very low volume equipment for applying pesticides in Africa and South East Asia. Reducing the volume of spray solution from 400 litres/ha to less than 50 litres/ha has transformed the economics of pesticide use but it also means that new formulations of old products need to be prepared and tested for their biological efficacy.

Conclusion

The key to success in any trials programme lies in the personal interactions between the people concerned and the two-way transmission of the data and ideas between the formulation chemist at one end, and the farmer at the other, with the biologists and physiologists in the middle. This two-way communication helps to ensure that ideas are constantly fed into the formulation development process, but it also means that close working relations are established with the users, ensuring that their requirements are not overlooked in the quest for the "perfect" formulation. A further bonus in this process is that problems in pest or disease control emcountered by farmers are fed back to the laboratory so that new active ingredients can be introduced to counter problems before they become epidemics.

The most critical stage for a pesticide manufacturing or formulating organism is the greenhouse testing because this is the period of intensive development work with new formulations being produced, tested for stability, storage and biological activity. A lot of data is generated at this stage which can be used to build up experience and understanding of the role of formulation adjuvants so that short cuts can be tried with the next compound. Background physiological research can help this process by rationalising the observations and bio-activity data.

Appendix - Low Volume Spraying

One of the major constraints to pesticide application by small farmers is the quantity of water required. This water may have to be carried to the field and then carried around the field in heavy knapsack sprayers. This usually requires one labourer to serve the water needs for two sprayers in the field. Time is also lost filling the spray tanks, a 15 litre conventional sprayer needs to be filled 27 times to apply 400 litres (per hectare) whereas a 5 litre ULV sprayer would only need 8 fillings to apply 40 litres. The extreme is with ULV drift spraying when one or two fillings only would be needed to spray 5 litres over a hectare.

The effectiveness of low volume spraying is based on the number of droplets generated. Most of the equipment uses spinning disc applicators which generate a very even sized droplet spectrum lacking the very large or very small droplets included in the spectrum of conventional sprayers. In the case of insecticides, in particular, the size can be reduced to give much more even cover resulting in considerable improvements in activity, X 2 being typical for insecticides. The biological advantages for herbicide application by ULV are much less clear but the economic advantages remain.

There are some interesting implications for the formulation chemist when conventional formulations are used at ULV rates. If a formulation has been designed so that the final surfactant concentration in 400 litres is 0.05%, then in 40 litres it will be 0.5%, and at 4 litres (ULV rate for drift application of insecticides) it will be 5%. Also when spraying at very low volumes it is possible to consider replacing the conventional formulations which are designed to be diluted with water with special non-dilutable formulations. For example, permethrin could be formulated as a solution in an organic solvent instead of an emulsifiable concentrate.

The technical requirements of ULV formulations may be more stringent for flowables which typically clog the spinning disc, but it is possible that in the absence of any need to add water more suspensions could be replaced with organic solvent solutions.

ANNEX 3

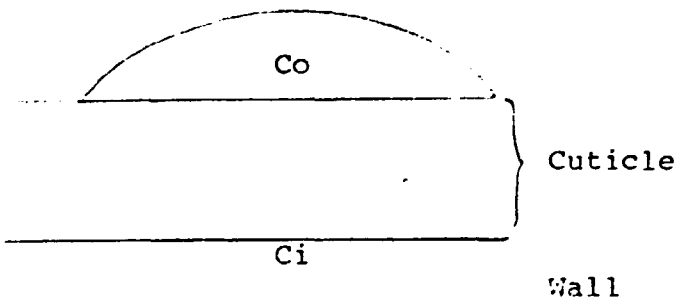
ADJUVANTS AND PESTICIDE UPTAKE

1 SURFACE EVENTS

It is generally accepted that pesticides cross the cuticle to enter plant tissue by diffusion. Ficks First Law states that the flux (J) of solute is dependent on the permeability coefficient (p) and the difference in concentration.

$$J = P (Co - Ci)$$

Where Co and Ci are the concentrations on the cutile surface and in the wall beneath the cutile respectively (Fig. 1) Flux (J) has the parameters of quantity of chemical, per unit area, per unit time, e.g. moles per square cm per second.



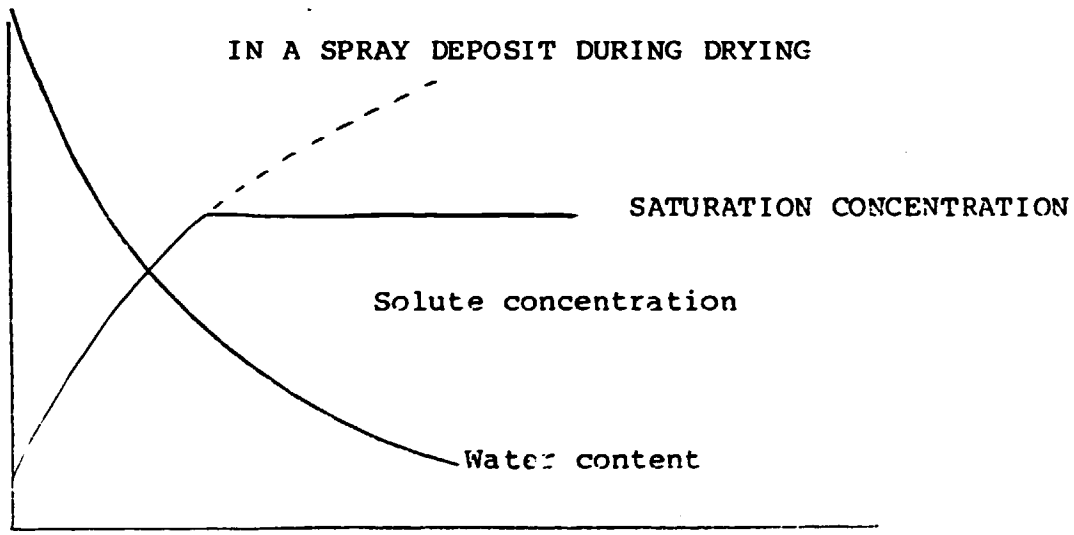
The uptake process can be considered from the point of view of the three compnoents of the equation, Co the external concentration, Ci the internal concentration and P the permeability characteristics of the cuticle. This report is concerned with the events within the droplet itself and factors which influence the external concentration of solutes (Co).

From the moment the spray droplets leave the spray jet they are losing water. The rate of water loss is determined by the water potential difference between the droplets (Ψd) and the surrounding air (Ψa). The air adjacent to the spray deposit may become saturated very rapidly so the rate of drying is largely controlled by the rate of movement of water from the saturated to the ambient air layers. Movement of air by wind or convection will reduce the thickness of the saturated layer and greatly increase the rate of drying. The behaviour of formulation components within the droplet are influenced by the rate of drying and by the ambient humidity.

As water is lost from the droplet, the concentration of solutes will increase. In the simplest case of a single solute in water, the concentration of the solute will continue to increase until the saturation point is reached, at which stage the compound will begin to precipitate. If the solute has significant solubility in water it will reduce the water potential of the solution by an amount proportional to its concentration. In this way, solutes, such as polar pesticides, humectants and high HLB surfactants, can greatly extend the period of drying (Fig. 2)

Figure 2

THEORETICAL CHANGES IN WATER CONTENT AND SOLUTE CONCENTRATION IN A SPRAY DEPOSIT DURING DRYING

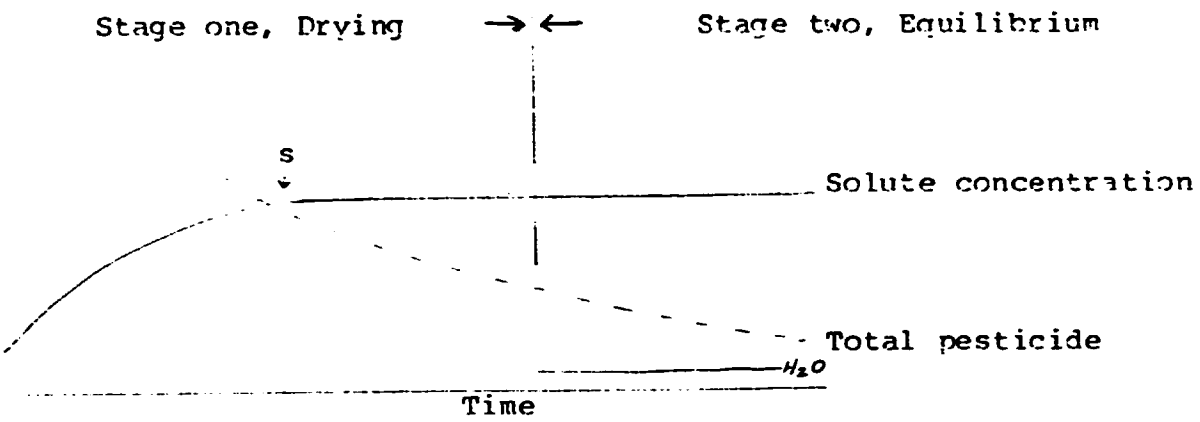


Under conditions of high humidity, some solutes may achieve equilibrium when there is a significant quantity of solvent remaining in the spray deposit (Fig 3). For example, many surfactants are able to retain their own weight of water at 100% ambient humudity. Such a high level of humidity is not unrealistic on the surface of a transpiring leaf within the crop canopy. Even if the deposit does dry out during the day, it is possible for it to take up water during the evening when humidity is much higher. In some situations the deposits may act as condensation nuclei for dew formation, leading to rewetting and possibly re-distribution of the spray deposit residues.

The rate of drying can be manipulated by formulation adjuvants, for example, adding a humectant or high HLB surfactant will slow the rate of drying and retain more water at equilibrium. This can directly affect the uptake of the pesticide into the plant, because total uptake includes the parameters of time and area of contact, as well as rate of movement.

Figure 3

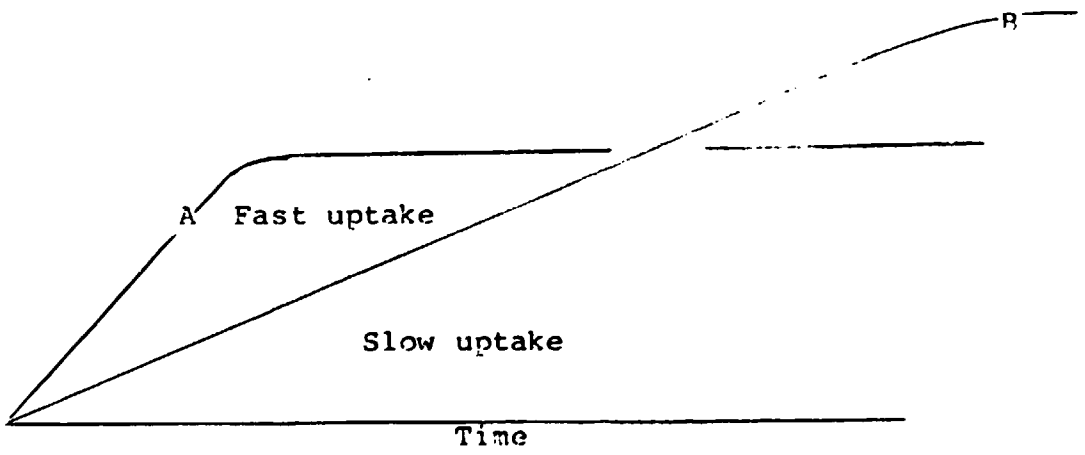
THE EQUILIBRIUM PHASE IN SPRAY DEPOSITS CONTAINING HYGROSCOPIC SOLUTES



s = saturation concentration

Figure 4

THE UPTAKE OF GIBERELLIC ACID INTO WHEAT LEAVES



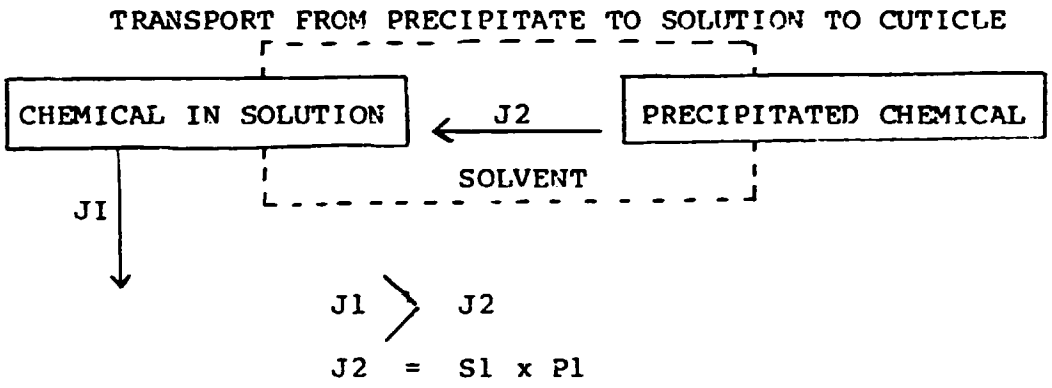
A = Aerosol OT formulation
B = Aerosol OT + sucrose formulation.

High humectant formulations have two potential effects on uptake, because they reduce the rate of water loss and hold more water at equilibrium, they may keep the active ingredient at a lower concentration and therefore result in slower uptake (B in figure 4). They also retain water for a much longer time and this can result in a longer period of uptake eventually giving higher total uptake (Fig. 4) In hot dry conditions, humectant effects can improve uptake, but the slower rate of penetration is a

disadvantage if there is rain because deposits remaining on the leaf are easily washed off.

Solid phase pesticide may be present in the spray solution, e.g. atrazine, or may form during droplet drying when the concentration exceeds the maximum solubility. Uptake from a solution containing a precipitate depends on the interaction between the precipitate and the solvent complex. If there is no interaction, i.e. the precipitate does not dissolve at all, then uptake is limited to the quantity of pesticide remaining in the solution. If the solute lost by diffusion into the cuticle is replaced by re-solution of the solid phase component then it becomes much more important to extend the period of drying in order to provide a mobile phase for solubilisation and uptake. During this stage of uptake the flux of solute from the precipitate to the solution (J2) becomes the rate limiting flux for uptake into the cuticle (Fig.5)

Figure 5



S1 = rate of dissolution of the chemical

P1 = rate of movement from the chemical solid-solution interface to the solution-cuticle interface

Cs = concentration of solute at the solid-solution interface

Dd = diffusion coefficient of the solute in the spray deposit.

Dd is not a constant parameter; it will vary with changes in temperature and viscosity of the solution and will therefore change as the composition of the deposit changes. This aspect can be manipulated by the selection of surfactants, solvents and humectants but the measurement of the physical properties of these solutions is difficult because the important changes take place when the deposits are almost dry and therefore very viscous.

The rate of solution of solid material is controlled by the physical properties of the pesticide e.g. water solubility and energy of crystallization, by the physical properties of the particle e.g. size and shape, and by the properties of the solvent. The properties of the solvent can be inherent to the solvent or contributed by other solutes. Inherent properties are concerned only with the solvent e.g. its viscosity and ability to dissolve the active ingredient, and can be changed by changing the solvent e.g. using an organic solvent instead of water in ULV formulations. The inherent properties of organic solvents are very important for the uptake of lipophylic compounds because they provide a mobile phase between the precipitate and the leaf surface. There is no equilibrium phase for these solvents, however, and once a solvent is lost by evaporation it cannot be replaced. Alternatively a non-drying solvent will give long term uptake but the active ingredient concentration may remain relatively low and the solvent may be lost from the surface by partitioning into the cuticle.

Contributed solvent properties are far more complex and amenable to change because they are produced by other components in the formulation. Surfactants are especially important in this respect because they are known to increase the solubility of organic components in water and can control the viscosity of the solution, and even its water content. Humectants and salts will also control the water content of the deposit and may modify the rate of precipitation of the active ingredient during the period of water loss.

The presence of solid particles in the spray deposit introduces heterogeneity in the distribution of the formulation components which becomes increasingly critical as water is lost from the deposit. Particles in the initial spray deposit will sediment at a rate dependent on their diameter (D), density (dp), the density of the solvent (ds) and the viscosity of the solvent (η) (Stokes Law)

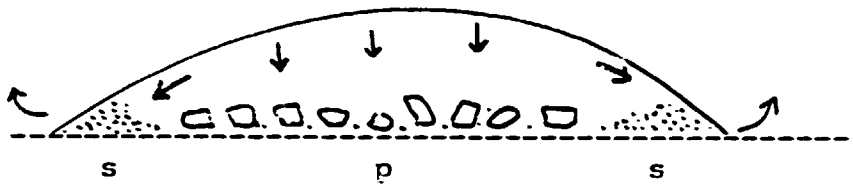
$$V = \frac{(dp - ds)\, g\, D^2}{18\, \eta}$$

g = acceleration due to gravity.

The effective diameter D will depend on other formulation components, such as dispersing agents and electrolytes, but as drying proceeds the concentration of these components will change, the particles will become more concentrated and the viscosity of the solvent will increase. Initial sedimentation of particles will be random throughout the volume of the droplet but water loss by evaporation is greatest at the circumference and it is here that secondary precipitates will be found (Figure 6).

Figure 6

PARTICLE DEPOSITION FROM A DRYING SPRAY DEPOSIT



s = Secondary deposits
p = Primary deposits

The secondary deposits include surfactants and humectants which means that there is a partial separation of the particles of pesticide from the water holding components of the formulation. The situation is most extreme in deposits formed from droplets with a low contact angle because the area of these deposits are much greater, leading to wider separation of the particles from the surfactant-rich circumference. Pesticide in the solid particles is less likely to enter solution when there is spatial separation of particles and surfactant.

Deposits on the leaf surface which have a large area relative to their initial volume and pesticide concentration have a lower quantity of pesticide per unit area. If the chemical solution is saturated, this may provide an initial advantage because there is a greater area over which uptake can occur , but a reduced quantity of formulation per unit area can have an adverse effect on long term pesticide uptake. The ability of a surfactant or an humectant to retain water is dependent on the intrinsic properties of the compound and on its environment. Surfactants exposed to low humidity ambient conditions may not be able to retain sufficient water at equilibrium to provide a mobile phase for pesticide solution and diffusion to the cuticle surface, but a three dimensional matrix of spray deposits will maintain a gradient of water from the near saturated conditions near the cuticle to the drier surface layers. Increasing the relative surface area of the droplet may reduce the concentration of the formulation components to the point that the gradient of humidity is too small to maintain sufficient moisture within the deposit to dissolve the active ingredient.

In conclusion, the changes that take place in the spray deposit as it dries on the leaf surface are complex and at present are not well quantified. It is clear, however, that formulation adjuvants can be used to optimise the uptake and distribution of pesticides on the plant leaf surface.

ANNEX 4

ADJUVANTS FOR PESTICIDES:

THE EFFECT OF MOLECULAR STRUCTURE ON UPTAKE

C.E. PRICE

The effective activity of a pesticide (A) is the product of its inherent activity (a) and its concentration at the site of action (c). For the purpose of this discussion, the site of action is within the plant, but strictly the site of action for a herbicide or plant growth regulator is within the cell and involves a number of additional stages which may reduce the effective activity. For this reason, high uptake of chemical into the plant is not always an indication of maximum activity.

Uptake differences between different pesticides into the same species can be important, even from a formulation designed to give efficient overall uptake and biological activity (Table 1).

Table 1

THE UPTAKE OF PACLOBUTRAZOL AND 1-METHYL PYRIDINIUM CLORIDE INTO SOYBEAN LEAVES

	Percentage uptake after 24 h
1-Methylpyridinium chloride	98
Paclobutrazol	26

There is no clear indication of what controls the uptake of compounds into a leaf. The main problem with this type of study is that a change to any one molecular parameter automatically changes another parameter, for instance, 2,4-D ester has greater lipid solubility than the salt but it also has lower water solubility and higher molecular weight.

Molecular properties must also be considered in relation to the plant species. The two related compounds, paclobutrazol and diclobutrazol differ only by one chlorine atom but uptake is quite different in some species (Table 2).

Table 2

THE UPTAKE OF PACLOBUTRAZOL INTO THREE PLANT SPECIES

	Cotton	Soybean	Cyperus rotundus
Paclobutrazol	47	26	47
Diclobutrazol	49	43	16

(Percentage uptake after 26 hours)

These data come from a series of experiments carried out under field conditions in southern Spain, in which ten compounds were applied to ten species and uptake measured after 26 hours. No single parameter controlled uptake but we found significant correlation between uptake and molecular dimensions (four species), molecular weight (three species) and aqueous solubility (two species). Partition coefficient and liquid solubility were only correlated with an uptake for a single species, Xanthiam pennsylvanicum, which is contrary to the widely held view that 2,4-D ester is better for foliar application than 2,4-D salt because it is able to penetrate into the plant more effectively. Part of the explanation may lie with the formulation used for the lipophylic and hydrophyilc compounds. Highly water soluble compounds, such as 2,4-D salts are usually applied to the plant as aqueous solutions containing just enough surfactant to wet the leaf surface, but lipid soluble compounds such as 2,4-D ester have to be applied in emulsions containing solvent and emulsifiers. Much of the higher activity of the esters can be attributed to these differences in formulation adjuvants. In an uptake experiment in which 2,4-D sodium salt and the isooctyl ester were applied in the same EC formulation, the salt form penetrated better than the ester in some species (Table 3).

Table 3

THE UPTAKE OF 2,4-D SALT AND ESTER INTO THREE SPECIES

Compounds	Ameranthus	Cyperus	Xanthium
2,4-D Salt	78	34	91
2,4-D Ester	78	59	60

Species: Ameranthus retroflexus
Cyperus rotundus
Xanthium pennsylvanicum

The 2,4-D salt will remain mainly in the aqueous phase of the emulsion while most of the ester will partition into the lipid phase. This means that the impact of an adjuvant will depend on the physical properties of the compound as well as the nature of the plant (Table 4)

Table 4

THE EFFECT OF SURFACTANTS ON THE UPTAKE OF ETHIRIMOL AND PERMETHRIN INTO LEAVES OF ORANGE

Surfactant		Permethrin	Ethirimol
Synperonic	A2*	80	36
"	A7*	68	65
"	A20*	31	40

*2,7 or 20 polyoxyethylene tridecyl ether
1% cyclohexanone was present in the permethrin formulation.

It is clear that uptake of permethrin is strongly favoured by the very low HLB surfactant Synperonic A2 while A7 is better for the more water soluble ethirimol. The log partition of ethrimol is 2.2 and if 1% cyclohexanone is added to the aqueous formulation it behaves more like permethrin in its response to surfactants (Table 5).

Table 5

THE EFFECT OF SURFACTANTS ON THE UPTAKE OF ETHIRIMOL AND PERMETHRIN FORMULATED WITH 1% CYCLOHEXANONE

Surfactant		Permethrin	Ethirimol
Synperonic	A2	80	68
"	A7	68	56
"	A20	31	28

Uptake into orange leaves after 26 hours.

Uptake data obtained after a single time interval can be misleading because short term effects are not always related to the long term total uptake. High HLB surfactants such as Synperonic A20 may act as humectants and enable uptake to continue for a longer period because water is retained in the deposit. More surprisingly Synperonic A20 can also prolong the uptake of water insoluble permethrin in the "dry" deposit (Table 6).

Table 6

THE UPTAKE OF PERMETHRIN INTO IPOMOEA AFTER ONE AND THREE DAYS

Surfactant	Percentage uptake		Percentage
	1 day	3 days	increase
Synperonic A2	64	70	17
Synperonic A7	56	66	23
" A20	47	70	43

* Percentage increase = $\frac{\text{Day 3} - \text{Day 1} \times 100}{100 - \text{Day 1}}$

2,4-D ester is an outstanding example of an active ingredient that is conjugated with an inert compound to produce a more active compound. The rational behind this modification of 2,4-D is that the more lipid soluble ester would penetrate the leaf cuticle more effectively, though we have seen that this explanation may be an oversimplification. The 2,4-D ester is not biologically active but must hydrolyse to release the active 2,4-D ion. The ester may undergo chemical hydrolysis but is more likely to be hydrolysed by esterase enzymes located in the cuticle or in the cell. If cell uptake is passive, the lipid soluble ester should cross the cell membrane more easily than the salt because it can establish a much higher concentration in the membrane. If it is then hydrolysed in the cell the salt form is less able to diffuse out. This scheme is complicated by the presence of an electrical potential gradient across the cell membrane, the cell being as much as 150 mv more negative inside compared with outside. The effect of this charge on the distribution of ions is given by the Nernst equation.

Nernst equation

$$E = \frac{RT}{zF} \log (Co/Ci)$$

E = cell potential (milli volts)
R = gas constant
T = absolute temperature
F = Faraday constant
z = valency of the ion
Co = concentration outside the cell
Ci = concentration inside the cell

At normal temperature and pressure $\frac{RT}{zF} = 25.249$

$\therefore$ Ln (Co/Ci) = E.z

If potential is - 150 mv and valency is 1.

$$\text{Ln } (Co/Ci) = \frac{150}{25.249}$$

$$= 5.9$$

$$Co/Ci = \exp 5.9$$

$$= 380$$

This means that for an anionic pesticide such as 2,4-D the external concentration will be 380 times greater than the internal concentration. The reverse is true of cations which achieve higher concentrations INSIDE the cell at equilibrium. If the above calculations are applied to a divalent cation such as paraquat the internal concentration may in theory be 100,000 times greater than the external concentration.

$$Ci/Co = \exp.(5.5 \times 2)$$

$$= 144590$$

Such concentration ratios are never normally achieved because paraquat rapidly destroys the cell membrane. The rapid herbicidal action of paraquat is a major cause of its poor translocation, and formulations have been made containing photosynthetic inhibitors such as diuron, which in theory should reduce the paraquat action which is dependent on photosynthesis. However, such formulations have not improved paraquat translocation because when paraquat herbicidal action is reduced it is accumulated by cells and therefore is still unable to translocate.

Attempts have been made to add other cations, to improve paraquat translocation (Table) and this is one of the few cases where cationic surfactants can give improved activity.

Table 7

THE EFFECT OF ORGANIC CATIONS ON PARAQUAT TRANSPORT IN WHEAT

Treatment solution	Percentages translocated
Paraquat 10^{-3} M	24
" " + choline chloride 10^{-3} M	31
" " + MPC 10^{-3} M	55

Relatively little work has been done on the relationship between molecular structure, plant species and formulation uptake. It is an area of great complexity but it may be the only way we will be able to explain exactly what controls uptake and translocation and what modification can be made to the formulation in order to optimise activity.

ANNEX 5

THE FREDERICK INSTITUTE

SEMINAR ON

"CURRENT THOUGHTS AND FUTURE TRENDS IN

PESTICIDE FORMULATIONS"

Date: April 5, 1986

Venue: Fippat, Padappai

A G E N D A

10.30 a.m.	:	Prayer
	:	Welcome address Mr. S. James Frederick (Chairman, Coromandel Indag Group)
	:	Inauguration of the seminar Hon'ble Thiru S. Thirunavukkarasu Minister for Food Govt. of Tamilnadu
	:	Presidential address Dr. G. Thyagarajan, Director Central Leather Research Institute
	:	Distribution of Awards
	:	Vote of thanks Mr. S. Ketharaman, Managing Director Indag Products Ltd.

TECHNICAL SESSION

Time: 12.00 hr

Venue: At board room, FIPPAT

Chairman	:	Dr. G. Rangaswami, President, FIPPAT
Rapporteur	:	Dr. R. Sundararajan
12.00 to 12.40 p.m.	:	Dr. Valkenburg - Role of Surfactants in Pesticide Formulations
12.40 to 1.15 p.m.	:	Mr. V. N. Dutta - Safety Aspects of Pesticides
1.15 p.m.	:	Lunch break
2.00 to 2.40 p.m.	:	Dr. Price - Bio-efficacy of formulations
2.40 to 3.40 p.m.	:	Dr. Khetan - Design of Pesticide Formulations
3.45 p.m.	:	General Discussions
4.00 p.m.	:	Concluding Remarks Dr. B. V. David, Director, FIPPAT

ANNEX 6

A N N A U N I V E R S I T Y

Madras 600 025

announces

HORIZONS IN BIOTECHNOLOGY

A series of seminars on the different facets of Biotechnology

Date : April 3, 1986; 3.00 - 5.00 p.m.

Venue : Seminar Hall, Department of Chemistry
College of Engineering

Title of Seminar:

Recent Trends in Formulation Technology of Biologicals
(sponsor: Coromandel Indag, Madras)

Participating Specialists:

1. Dr. Susheel Khetan

   Head PDPI and Director, R & D Hindhustan Insecticides Ltd., Gurgaon, New Delhi .... Ph.D (Organic Chemistry, IIT, Kanpur),
   Specialization: Pesticide formulation designs.

2. Dr. Wade Van Valkenberg

   3M Company, St. Louis, Minnesota, USA
   Ph.D. (Colloid and surface chemistry)
   Specialization: Pesticide formulation/micro encapsulation

3. Dr. Clive Elsworth Price
   Imperial College, London.
   Specialization: Ph.D. (Plant Physiology).
   Role of adjuvents in Bioefficasy of Pesticide formulations.

We cordially invite you and your colleagues to attend the seminar.

Yours sincerely,

KUNTHALA JAYARAMAN
Professor of Biotechnology
A.C. College of Technology
Madras 600 025
Tel.: (044) 414240