SESSION 4A

TOPICS IN PEST AND DISEASE MANAGEMENT IN WARM CLIMATES

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CONTROL OF GRASSHOPPERS AND MIGRATORY LOCUSTS

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ABSTRACT

During 1986 and 1987 countries in the Sahel suffered from outbreaks of various grasshopper species, in particular the Senegalese grasshopper, *Oedaleus senegalensis*. These necessitated wide-scale control campaigns and about five million hectares were treated. These campaigns were successful to the extent that major crop damage was avoided, but the overall cost was over US$60 million. During the same period a new Desert Locust plague developed and is now threatening crops in most countries in Africa north of the Equator and in the Near East. It has reached such proportions that it will take at least two to three years before it is brought under control. FAO is coordinating the control campaigns through its Emergency Centre for Locust Operations (ECLO). For the same purpose, National Steering Committees have been established in the countries. The use of pesticides is discussed briefly, including the withdrawal of dieldrin for the control of Desert Locust hoppers.

INTRODUCTION

The return of near normal rains to much of Africa in 1985, after a number of relatively dry years, resulted in the simultaneous development of widespread infestations of grasshoppers in West Africa and of increased populations of four species of migratory locusts in Eastern, Central and Southern Africa for the first time in 50 years. The upsurges of the Brown Locust, the Red Locust and the African Migratory Locust stayed rather limited in space and time. But the grasshopper infestations seriously affected most of the Sahel countries during 1986 and 1987, while the Desert Locust has, over the last three years, attained plague proportions threatening virtually all countries in Africa north of the Equator, as well as those in the Near East.

The main grasshopper species in the Sahel was the Senegalese grasshopper, *Oedaleus senegalensis*, particularly in the northern Sahel, but there were also widespread infestations of *Kraussaria angulifera*, *Hierglyphus* spp. and, in the more humid zone, of *Zonocerus variegatus*. These are basically national pests, and a chronic problem. They do not migrate great distances, only following the Inter-Tropical Convergence Zone north and south with the progress of the season. Grasshoppers are polyphagous insects attacking a wide range of plants. The Sahel has huge uncultivated areas and the biggest danger grasshoppers pose is when climatic conditions result in the large numbers of insects in the wild vegetation invading the crops.

The Desert Locust, *Schistocerca gregaria*, the most dangerous migratory locust species, on the other hand, is an international threat in a belt from the Indian sub-continent to the Atlantic coast of West Africa. In times of recession, small numbers of insects live scattered over the deserts of the region. When rain falls and vegetation appears in an area where there are locusts, their numbers can increase extremely rapidly. They then become gregarious and ultimately migrate in swarms down the prevailing winds, sometimes great distances, into agricultural areas where they can do immense damage. Favourable conditions in the areas they invade then maintain the plague.

There are, of course, many similarities between grasshoppers and locusts. For both, rains, especially good rains after long drought (as in 1974 and 1985), are the key factor setting off an upsurge, probably because the populations increase faster than their natural parasites and predators. Both can cause significant damage to a large variety of plants, eating daily their own weight in green vegetation. The same pesticides and

equipment are used against both, but the control strategies are very different.

Grasshoppers are combatted at national level, by national crop protection services, and the strategy is to protect crops, not overall population reduction. This means equipping farmers early in the season (usually with dusts) to control hoppers in their crops, and intervening with greater means against migrating winged adults with rapidly-acting pesticides later in the season when they threaten crops. Whether control is economically worthwhile is a function of the crops at risk; very often it is not. The strategy against the Desert Locust is survey and preventive control, that is to permanently monitor the vast recession area for rainfall and vegetation which might favour reproduction and to intervene to destroy populations which have become gregarious. The strategy is international and aims at preventing plagues, not protecting crops (at least during recession periods).

THE GRASSHOPPER CONTROL CAMPAIGNS IN THE SAHEL

Following the drought years of 1982-84 there were good rains in much of the Sahel in 1985 and, as in 1974, following the drought of 1968-73, there was a rapid increase in the population levels of many species of grasshopper, most notably the Senegalese grasshopper, *Oedaleus senegalensis*. On the basis of field reports, the Government of Mali and FAO launched an emergency campaign, supplemented by contributions from the European Economic Community, France, the Federal Republic of Germany, UNDP and USAID. In September and October 1985 aerial and ground control operations were mounted against adult populations returning south at the end of the rainy season and threatening ripening sorghum and millet crops, particularly in Mali and Burkina Faso. Some 200,000 hectares of infestations were treated but there was widespread egg-laying before the onset of the dry season.

In January 1986, the Director General of FAO brought to the attention of the international community the urgent need to prepare for an extensive campaign in 1986 and the volume of external assistance which would be needed to implement it. A donor meeting was held in Rome on 7 May 1986 to seek the necessary support. The participants at the meeting agreed that FAO should coordinate the campaigns and the technical and material assistance required for them.

In conformity with the strategy adopted in late 1985, the 1986 grasshopper control campaign was executed in two phases: the first, from May to August, aimed at the protection of newly established crops at the beginning of the rainy season by the application of insecticidal dusts, mainly by farmers themselves; the second phase aimed at preventing damage to maturing crops in September and October by aerial spraying operations in particular. During Phase I, about 700,000 hectares were treated, but a very large proportion of the population remained uncontrolled, necessitating a much larger Phase II of the campaign. Thus, an additional 2,600,000 hectares were treated mainly through the use of fixed-wing spraying aircraft to apply concentrated liquid insecticides. In all, 39 aircraft were involved ranging in spraying capacity from 300 to 11,250 litres. Aerial spraying commenced in early September and was largely concluded by the end of October. The campaign could be considered successful as crop losses were very limited, of the order of 2 - 3 percent only. The overall assistance amounted to slightly over US$30 million; the cost per hectare treated was US$9.10.

Egg-pod surveys during the 1986-87 dry season and observations of laying adults at the end of the 1986 rainy season indicated that major infestations could occur again in 1987. But, during a planning meeting held in Rome in December 1986, it was emphasised that the extent and intensity of the 1987 infestations would be largely dependent upon rainfall. The main infestations early in the season were in Chad, where young crops were completely destroyed in some areas, and in northern Nigeria where some nymphal bands formed in early June. Rainfall during June and July was patchy throughout the Sahel and, as a result, the infestations were considerably lighter than had been forecast. Heavy mortality was observed among recently hatched nymphs due to lack of food. Earlier, parasitism and predation had caused considerable mortality of overwintering eggs. First generation adults appeared from late June but these tended to move south rather than north as the Inter-Tropical Convergence Zone lay to the south of its normal position for that time of year.

Phase I control operations were undertaken in many areas but on a rather limited scale. There were good rains in September, which resulted in widespread late infestations in the Mauritania-Mali border areas, central-southern Niger and in Chad. These necessitated large scale aerial spraying which raised the total area treated to over 1,750,000 hectares.

The assistance provided by donors during 1987 amounted to some US$32 million, i.e. an almost similar amount to that provided in 1986. The total area treated was about half of that treated in 1986. However, an evaluation meeting of the campaign, held on 8 - 9 December 1987 in Rome, considered that it was wrong to conclude that the 1987 operations had been twice as costly as in 1986, on the contrary, there was much evidence that in 1987 operations were more effective and there was less wastage of pesticides. Considerable stocks of pesticides were present in the countries at the end of the 1987 control campaign.

During 1988, limited upsurges of grasshoppers continued to occur in the Sahel region, but this should be considered as a normal situation for this type of insect.

INTERNATIONAL CAMPAIGN FOR DESERT LOCUST CONTROL

The present Desert Locust plague has its origin in the favourable breeding conditions around the Red Sea in late 1985. This gave rise to reproduction on both sides of the Red Sea coast and control operations were carried out in Saudi Arabia, Sudan and Ethiopia. In July and August 1986 small swarms moved westwards across northern Sudan but this movement of the Desert Locust went largely unnoticed. In the summer of 1987, there were good early rains which allowed these escapes to find favourable breeding grounds, in particular in north-eastern Chad, in the Ennedi area. Large scale infestations developed and, in July 1987, a warning was issued and control operations were prepared and undertaken. However, the inaccessibility of a large part of the area and the limited effectiveness of the pesticides used did not lead to adequate control.

Strong easterly winds during October and November 1987 pushed the swarms that had developed westwards, and northern Mauritania, western Sahara, east Morocco and south-western Algeria were invaded. The same winds also brought rains and, thus, favourable breeding conditions for the Desert Locust. The favourable conditions in these areas lasted for about five months, from October 1987 to March 1988. Extensive control operations were mounted but these did not lead to complete control for three major reasons: i) continuous favourable breeding conditions; ii) limited effectiveness of the pesticides used; and iii) the inaccessibility of certain parts of the infested areas. From early March onwards, newly developed swarms moved in northern and north-eastern directions, further invading Morocco, Algeria, Tunisia and Libya. In late March the Cape Verde Islands were also invaded.

In the north-west African countries, about 2 to 3 million hectares were probably infested from March 1988 onwards and, although extensive control operations were undertaken, egg laying occurred on a large scale and a new generation of adults developed. Based on information from earlier plague situations, it was expected that countries south of the Sahara would be invaded only during May-June by swarms moving south with the predominant winds. However, this movement took place from early April onwards. At that time swarms reached the Senegal river valley and spread over Senegal, southern Mauritania and western Mali. Extensive breeding in the southern part of north-west Africa was probably the main reason for this. Early in August, hopper bands were found in most of the Sahel area and small swarms were encountered at various places. Of greatest concern were very heavy infestations in north-eastern Chad, as well as in the border area between Niger and Chad, each covering about 3 million hectares.

From late May, swarms invaded Sudan from the west and by mid-July large mature swarms reached as far east as Ethiopia. Extensive breeding occurred in the western province of Darfur, in the Khartoum area and probably also in the eastern Kassala province. Large mature swarms, up to 150 km^2, were seen in Sudan in July and it must be assumed that all these bred successfully. In Ethiopia, approximately 20 small mature swarms were present in the Asmara area from late July. As heavy rains fell in the first half of August it must be assumed that successful breeding occurred and that hopper bands will form during late August.

In a special donor meeting held in Rome on 11 August 1988, the possible area requiring control in Chad, Sudan and Ethiopia was estimated as follows:

Country	Minimum area (ha)	Maximum area (ha)
Chad	2 000 000	3 000 000
Sudan	1 000 000	2 500 000
Ethiopia	250 000	500 000
Total	3 250 000	6 000 000

Most of the control of the current Desert Locust plague has been done by aerial application of pesticides. At the height of the invasion in Morocco, Algeria and Tunisia in spring 1988 over 90 aircraft were used. In total, more than 5 million hectares were sprayed in these countries from the beginning of the invasion in October 1987 and this region was virtually free of Desert Locust from August onwards. Since July control operations have been undertaken in the Sahel area, and in Sudan and Ethiopia.

In north-west Africa, control has been undertaken by national control units. In the Sahel, a two-pronged approach is carried out, which consists of: i) control operations by national units; the responsibility for these falls under the national plant protection services, and ii) a regional aerial control unit under FAO supervision which assists in countries where the infestations go beyond the national capabilities.

There are no signs as yet that this Desert Locust plague can be stopped in the near future. On the contrary, given the current extent of the invasion, it is most likely that it will last at least for another two to three years. The current infestation in Chad and Sudan is estimated to be about ten times as large as the one at the same time last year. This shows the magnitude of the development of the plague. It means in particular that, from October onwards, the north-west African countries will be invaded again. Moreover, the plague will in all probability extend further into East Africa and the Near East.

Campaign costs are very high and by August 1988 they were already in the order of US$150 million; donor support has been extremely generous and has already amounted to over US$80 million. But it may become increasingly difficult to obtain the necessary support if the plague continues for a long period of time. However, if adequate control capability cannot be maintained, the Desert Locust itself will become the best fund raiser by the havoc it will undoubtedly create.

OVERALL ORGANIZATION OF CONTROL CAMPAIGNS

The implementation of the control campaigns falls under the direct responsibility of the countries affected. Regional inter-governmental structures have been created to provide the necessary support for this. This has taken different forms; in north-west Africa the countries have relatively strong national units and cooperation is promoted through the FAO Commission for Controlling the Desert Locust in North West Africa. In west and east Africa national units are relatively weak and Regional Control Organizations exist (OCLALAV and DLCO-EA) that are supposed to carry out control operations in the member countries. However, these organizations lack the means to do so effectively.

Given this situation, the emergency control campaigns required the establishment of special mechanisms to ensure effective and timely support. These arrangements have been made at three levels: by the countries affected, and by multilateral and donor agencies. In the affected countries, National Steering Committees have been established, comprising government and donor representatives, as well as FAO. These Committees appraise the grasshopper/locust situation, identify needs and advise on survey and control operations. The findings of the Committees are regularly transmitted to FAO and the donors.

In order to better support the emergency campaigns, FAO established in August 1986 the Emergency

Centre for Locust Operations (ECLO). Based on country reports received, ECLO makes an overall analysis of the situation, prepares forecasts on the possible development of the grasshopper and Desert Locust invasions, reviews needs and ensures liaison with all parties concerned through its telexed ECLO Bulletin and other contacts. ECLO also implements directly control campaign activities with funds received from various donors. The donor agencies review needs at their Headquarters and provide financial and material support according to priorities adopted, mostly directly to the countries concerned.

PESTICIDES AND RELATED PROBLEMS

A very important aspect of the Desert Locust control campaign is the use of pesticides and, in that respect, it is essential to emphasise that the requirements to control swarms of adults are different from those for larvae control. For adult control there is a need for rapidly acting pesticides that do not need to be very persistent. For many years the pesticides used were either organophosphates or carbamates; more recently, the synthetic pyrethroids have been added. Pesticides currently recommended are given in Table 1.

TABLE 1

Pesticides recommended for grasshopper and migratory locust control

Product	Formulation (ULV)	Dose (l/ha)
fenitrothion	50%	1
	96%	0.5
malathion	96%	1
diazinon	90%	1
lambdacyhalothrin	40 g/l	0.5
fenitrothion	245 g/l	1
+ esfenvalerate	5 g/l	
lindane	250 g/l	1
+ lambdacyhalothrin	10 g/l	1
chlorpyrifos	240 g/l	1
	450 g/l	0.5

For the control of larvae (hoppers), which can emerge over a period of 2 - 3 weeks from the eggs laid in the ground, there is a need for a persistent pesticide in order to avoid repeated applications. As hoppers move in bands, the technique developed during the last plague in the 1950s was the so-called barrier spraying with dieldrin. By this method strips of land and vegetation over which the hoppers would move were sprayed with dieldrin, with only 10 percent of the area being covered and only 20 - 40 g/ha a.i. applied. This method was extremely effective, virtually eliminating the existing hopper populations.

With the changing views on the use of persistent pesticides, the use of dieldrin for Desert Locust control has come under severe criticism and, given the fact that most countries - both the ones affected by the Desert Locust as well as the donors - have banned the use of dieldrin, we are now obliged to apply less persistent chemicals and these are the same as those recommended for adult control. In general, the effectiveness of these chemicals is less than dieldrin and this may lead to insufficient control. For example, a 90 percent kill may be considered as quite successful but that still leaves 10 percent of the population. Given the effect of a multiplication factor of at least 10 per generation, it means that the new generation is still as big, if not bigger, than the preceding one. The withdrawal of dieldrin has had the additional effect that the control costs have increased about tenfold.

CONCLUSION

The last major Desert Locust plague lasted 13 years, from 1950 to 1963. The areas infested by August 1988 were larger than at any time during that event, and consequently the current plague must be considered as extremely serious. At this stage, there is no indication yet that it can be brought under control within a short period of time. Control efforts will have to be aimed in particular at reducing damage that may be caused to crops. The countries concerned will be unable to finance the extensive operations required. Up till now, the north African countries have paid over 80 percent of the control costs, but this figure is usually less than 20 percent for most of the other countries involved and very extensive external support will continue to be required.

Although these emergency operations will need all possible attention, the medium-term needs for effective preventative control of the Desert Locust should be considered at the same time. The events that led to the current plague situation need to be analysed and the necessary lessons drawn should serve as a basis to strengthen current structures and develop new ones. For Desert Locust control it is quite clear that regional structures are needed. But these can only operate effectively when, at the national level, well functioning units exist and medium-term support should be directed to this in the near future.

Research needs must also be reviewed. The ban on dieldrin should be an incentive to study new control approaches, including the more selective use of pesticides and biological control. Monitoring and forecasting of Desert Locust populations are essential activities for effective control and should be further improved. For this, increased use will need to be made of satellite imagery and data processing facilities.

The current plague constitutes a major threat to the economies of many African and Near East countries. It will require for a significant period of time a very strong international cooperative effort to ensure that major food losses do not occur and that local populations do not suffer. This effort is also required to safeguard earlier investments in agricultural production improvements and to avoid environmental degradation.

PEST MANAGEMENT ISSUES - FOOD CROPS IN DEVELOPING COUNTRIES

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ABSTRACT

Improvements in agricultural technology, including pest management, have resulted in the production of more food than we can eat in Europe. However, in some areas of the developing world, human populations have outstripped increases in food production and a considerable proportion of the crops are lost to pests. Research aimed at reducing pest caused losses has been carried out through many national and international agencies for several decades. Unfortunately, most of this research has been uncoordinated and has resulted in little or no impact in farmers' fields. The only impact that is widely evident is an increasing use of chemical pesticides, sometimes with deleterious effects. The problems of potential alternatives, or supplements, to insecticide use, including biocontrol and host plant resistance, are briefly described, with special reference to *Heliothis armigera*. The need for greater accountability of research is stressed and it is suggested that more attention should be paid to the interdisciplinary team approach, with increased experimentation in farmers' fields.

INTRODUCTION

Our climate, but particularly the winters, generally limits insect damage to crops in northern Europe. But, 40 years ago, we were adept in biting into apples with care, to avoid the maggot that probably lurked in the core, in discarding peas that contained grubs, and in soaking cauliflowers in salt water to drive out caterpillars. Now, we would complain to our greengrocer if we found any insect in our fruit and vegetables and many of our children have not seen insect contaminated food. This change, largely due to the judicious use of insecticides, is part of the broad advance of agricultural technology, which has resulted in large increases in productivity. Supplies of most foods now exceeds demand and we have mountains of surplus produce.

In the developing countries, most of which are in the warmer regions of the world, the situation is very different. There the climates are generally more favourable for insect multiplication and in some areas human population increase has outpaced agricultural production. For many children, fruit and vegetables are rarely tasted luxuries, with or without insects.

Prior to the introduction of modern technology, including insecticide use, natural selection ensured that farmers developed farming systems that limited pest losses through a form of integrated pest management that is seldom appreciated. In particular, the strict observance of appropriate seasons for each crop was of great importance. Such farming systems were not highly productive, but gave relatively stable sustenance to the farmer and his family through good and bad seasons.

Increasing human populations and urbanization in the developing countries require that farmers should now produce not only enough to feed their own families, but also sufficient surplus to feed the rapidly increasing numbers of families in the cities. The old, evolved, farming systems are not productive enough for the modern needs.

GREEN REVOLUTION

It is not difficult to increase productivity through the introduction of fertilizers, irrigation, new crop

varieties and improved agronomy, provided the insect pest problems can be controlled. But there has been great variation in progress towards increased productivity across the many developing countries and crops that are grown. For example, the well publicised green revolution has converted India from a large net importer of food grains in the 1960s to a country with very large reserves of grain in the 1980s. This green revolution was mainly in wheat and rice production and was the result of new, high yielding varieties, increased use of fertilizers and irrigation, and sound economic and social policies, particularly in marketing. Improved pest control played only a small role in this revolution, for these crops, particularly wheat in northern India, have relatively few major pest problems. In contrast, there has been no green revolution in the production of legumes in India and there is a very large shortfall in their supply, in spite of great efforts by the Government of India. India's major legumes, groundnuts, pigeonpeas and chickpeas, are particularl y prone to pests and diseases and farmers have found that attempts to increase the production of these crops are very risky. Even after using all of the recommended inputs, including pesticides, farmers have found that pests or diseases may wipe out these crops (Reed, 1987).

With such variations in pest management problems between crops in a single country, generalisations concerning pest management issues on food crops in developing countries have obvious limitations. However, this presentation is an attempt to highlight some general issues as perceived by one who has recently retired from a career in pest management research, first on cotton in Africa and India, and then on food legumes at the International Crops Research Institute for the Semi-Arid Tropic (ICRISAT). This is one of the International Agricultural Research Centres (IARCs) established with the primary object of increasing food supplies in the developing world. *Heliothis armigera*, a well known pest that attacks cotton, legumes and many other crops in Africa and Asia, will be used as an example to illustrate the issues.

ENTOMOLOGY RESEARCH IN DEVELOPING COUNTRIES

Agricultural entomology is a recent import to most developing countries. Even India, the cradle of many sciences, had virtually no entomology tradition prior to the arrival of the Imperial Entomologists early in the 20th Century. In many developing countries, the first agricultural entomologists were imported through various European
colonial agencies with the primary objective of increasing the production of exportable cash crops. Thus, much of the early research was directed towards commodities, with entomologists as members of teams that included breeders, agronomists and pathologists.

By the 1950s, there had been a considerable expansion of plant protection research in developing countries, with several agencies employing entomologists from the developed world. Some specialist agencies directed their efforts towards individual pests such as locusts and tsetse and others to specific facets such as biological control and pesticide use. Greater efforts were being directed towards food crops through the Food and Agriculture Organisation (FAO) and bilateral aid organisations. By this time, several countries had their own entomologists, some having trained in Europe and others in the local colleges and universities. Newly available synthetic insecticides were seen by many to be the answer to most pest problems. Agricultural entomologists invested much of their time on insecticide trials, either because they perceived that such work was likely to be the most productive, or because they were directed to do so by the administrators who pressed for short term productive research and development. In the next 20 years agricultural insecticide use expanded rapidly in many of the developing countries with more than half being used on cotton.

In the 1970s, problems resulting from the injudicious use of insecticides, particularly on cotton in the Americas (Adkisson 1971) had received extensive publicity and the modern concept of Integrated Pest Management (IPM) became popular, in words if not in deeds. Many agricultural entomologists now eagerly sought alternatives to insecticide based research, some in well planned programmes, but others in a series of short term excursions.

Consequently, in the 1980s, pest management research and development presents a very diverse and uncoordinated picture across and within the developing countries. At one extreme is India with several hundred entomologists, trained within the country and employed in a variety of national and state institutions. At the other extreme are the many countries with no, or very few, entomologists. Pest

management research is perceived as having great potential from a small input, so several developed countries sponsor such research as part of their aid to the developing world. Many itinerant professionals are employed in such aid schemes, spending varying proportions of their time in their home countries and in the developing countries. Is such research good value? How can we measure the cost:benefit ratios?

RESEARCH ACCOUNTABILITY

The final objective of agricultural research, including that in pest management, must be to improve the profitability of farming. Here, profit is intended in a wide sense, not just to include cash returns, but also improvements in the quality of life of those who work on the farms and increases in the supply and quality of agricultural products, but without deterioration in the land and environment.

Most agricultural, and pest management, research is essentially long term so we can claim many years grace before the ultimate success of most research can be audited. For interim evidence of progress we rely upon reports of laboratory and research station field trials that appear in annual reports and in national and international journals.

It is clear that a large proportion of research efforts never reaches any form of report. Much appears only in restricted circulation reports that are ephemeral and disappear without trace. A continually escalating number of journals are filled with interim evidence of progress, and computer tapes are full of undigested data collected at great expense. Such interim evidence allows the promotion of "productive scientists" and expansion of funding to their projects. Unfortunately, those who look beyond these piles of paper will search in vain in the farmers' fields for any evidence of impact from most research projects. It may be useful to review briefly the research into the major components of pest management and to predict its future utility.

INSECTICIDES

Farmers in developing countries face many varied problems in the adoption of insecticide use. There are often local shortages of appropriate insecticides and some may be contaminated. Insecticides have to be purchased during the crop growth season when cash and credit may be in short supply. Cheap application equipment is unreliable and spraying or dusting can be hard and unpleasant work. However, in spite of these and many other hurdles, the use of insecticides is growing rapidly in many developing countries. For example agricultural insecticide consumption in India increased from 39,000 tonnes in 1974 to 62,000 tonnes in 1984. In terms of area treated, that increase is greater than apparent, for insecticides such as DDT, which were applied at a kilogramme or more per hectare, are being replaced by chemicals such as the synthetic pyrethroids, which are applied at much lower dosages (David 1986).

In many countries the farmers were first encouraged to use insecticides on their cash crops with subsidies applied to chemicals and applicators. In countries where good internal markets have developed, and where farmers receive much of the money that the consumers pay for their food, the distinction between cash and food crops has become increasingly blurred, for food production can become more lucrative than cotton. In those countries farmers have found profit in using insecticides on some of their food crops, often without the encouragement, or knowledge, of the administrators. Statistics of insecticide use on individual food crops are rarely available and where they are, are probably grossly inaccurate. There is obvious danger in using insecticides intended for the non-edible cash crops on food crops. There are few, if any, checks on the pesticide contents of foods sold in the markets of most developing countries. Where checks have been made, green vegetables, in particular, have often been found to have unacceptable residue levels.

There is a wide divergence between the entomologists' and the farmers' views of a "good insecticide". Most entomologists would like an agricultural insecticide to be non-persistent and specific to the key pest, so leaving the beneficial fauna intact. Thus, for example, DDT was a "bad insecticide" for it was persistent and killed the natural enemies of aphids and mites, so promoting damaging outbreaks by these secondary pests. From the farmer's viewpoint, an insecticide should be cheap, effective and long-lasting, to avoid the need for frequent application. DDT fulfilled these criteria, but would have been even better if it had a wider

spectrum and had killed the aphids and mites! The key pest concept is not easily appreciated by farmers, particularly on crops such as cotton, pigeonpea and groundnuts where any one of a dozen or morepests may badly damage the crop. The need for a range of relatively specific insecticides increases costs. If wide spectrum insecticides are not available, the farmers will mix cocktails to ensure that both chewing and sucking pests are controlled in one application. In southern India in the 1970s it was not unusual to find farmers who had escalated insecticide use to 20 or more cocktail sprays on a cotton crop.

The eventual consequences of such concepts and practices were predictable, and by 1987 there was good evidence that H.armigera could not be controlled by any available pesticide, including the synthetic pyrethroids, in one of the major cotton growing areas of India. This was bad news, not just for cotton, but for the many food crops on which *H.armigera* feeds.

BIOLOGICAL CONTROL

Using good insects to kill the bad ones is a splendid prospect that has great appeal and has provided many entomologists with a lifetime of interest and travel. There have been many genuine successes in the inoculative introduction of exotic parasites and predators. There are also reports of success in the use of inundative releases of parasites such as *Trichogramma* spp. Viruses and other micro-organisms that kill insects can be mass produced and sprayed as biological insecticides. However, there is little sign of the widespread use, or even potential, of biocontrol in farmers' fields.

In southern India more than 25 species of parasitoids have been found in *H.armigera* (Bhatnagar et al 1982). This pest is also preyed upon by many species of insects and other animals. It has often been alleged that *Heliothis* spp are unnecessary pests that have been promoted by insecticide use that has killed these natural enemies. However, in a large pesticide-free area of ICRISAT in southern India, *H.armigera* builtup to damaging levels on pigeonpea in every year from 1978 to 1988 in spite of the many natural enemies. Attempts to supplement these with exotic inundations and inundative releases of *Trichogramma* were ineffective.

The use of insect diseases that are relatively specific would appear to offer considerable potential in pest management on food crops (Burges 1981). Over the last 20 years there have been many reports that a nuclear polyhedrosis virus (NPV) can provide a good safe means of *Heliothis* control. This virus has been marketed in several countries, but production has been discontinued in the USA; good evidence of lack of profit. In China, the village scale production of such viruses is said to be thriving. However, in India such developments are viewed with caution. Spraying the ground-up bodies of virus-killed larvae on food crops may provide a cheap and effective means of *H.armigera* control, but evidence that the dead insects contains no organisms that would threaten the health of man and the thriving sericulture industry is required. In any case, a series of field tests with the virus at ICRISAT gave only 60% kill of *H.armigera*, and resulted in more damage and lower yields than in insecticide treated crops.

HOST PLANT RESISTANCE

The ideal form of pest control would be through the growing of crops that are avoided by insects but are edible and nutritious for man. Although this is impossible, plants with resistance to the major pestshave been found wherever a determined search of the germplasm has been made. Thus, at ICRISAT, we have selected pigeonpea and chickpea plants that have considerable resistance to *H.armigera*, and groundnuts and sorghum plants with resistance to their major pests have also been identified.

Several such resistances have been found and reported in the past, but very few have been exploited and reached the farmer. For example, reports of sporadic research going back over 50 years revealed useful levels of resistance to several of the major pests of peas, but there appears to have been no commercial releases of seed that claimed to contain these reported resistances (Reed et al 1986).

It is most unlikely that a resistant plant plucked from the germplasm will contain all of the other characters required in a productive crop. For example, the chickpeas and pigeonpeas selected for resistance to *H.armigera*

were very susceptible to fusarium wilt. A crossing programme between these plants and fusarium resistant selections has now produced progeny that are resistant to both the pest and the disease. It is hoped that further selection will lead to plants that will give good yields in farmers' fields with little or no pesticide use.

The successful exploitation of host plant resistance requires well planned, determined and persistent collaboration between entomologists, plant breeders and other scientists over many years. Such research is not cheap, and cannot be afforded by individual national efforts in most developing countries. The only possible vehicles for such research are the International Agricultural Research Centres or the multinational agrochemical companies that have added seed companies to their plant protection activities.

Host plant resistance has been successfully and widely used to control diseases in many crops, so why has there been so little effort towards breeding for resistance to insect pests? The insecticide success story has stifled such work, so plant breeder/pathologist teams are common, while entomologists sit in separate laboratories chasing other wild geese.

INTEGRATED PEST MANAGEMENT

Insecticide resistant *Heliothis* spp provided the ammunition for the IPM crusade. This succeeded in arousing public awareness of the potential problems of insecticide use and provided impetus to research on alternative control components. However, the honeymoon period has long since ended and cynics point to the continued successful reliance upon pesticides as evidence that IPM will continue to be an attractive but sophisticated concept, rather than a widely practiced operation.

Insecticides are being increasingly used on food crops in the developing countries, but there is at least a general awareness that they should not be used indiscriminately. Perhaps the most encouraging development is that there are widespread attempts to encourage insecticide use according to need, rather than according to the calendar or phenotypic development of the crop. This is the first vital step towards practicable IPM. Unfortunately it also appears to be the only advance that we have readily available for most crops in the immediate future. Even this simple measure is not without problems. Scouting for pests and simple threshold action is not easily popularised. Needs based insecticide use may result in very uneven demands for chemicals across areas and seasons, so increasing problems for manufacturers and local stockists, with inevitable price increases to compensate for theincreased risks.

THE GAP BETWEEN RESEARCH STATIONS AND FARMERS' FIELDS

In developed countries, crop yields in farmers' fields are generally similar to, or may even exceed, those on the research stations. In developing countries, many research stations commonly report yields that are many times greater than those in farmers' fields. Such differences can be interpreted in many ways, butthe most obvious conclusion is that there is a failure in extending research results to farmers and that continued investment in research may be of doubtful value. The much maligned extension services have traditionally been the scapegoats for such failures. However, most farmers are not fools and they will actively seek out advances that are profitable, even if the extension services are less than energetic.

The unfortunate fact is that crops grown on most research stations in developing countries are grown with inputs that are either unavailable or not profitable for most local farmers. Much research utilises imported chemicals and machinery that will never reach the village store. Most research station farms have long since become totally atypical of the surrounding farmers' fields and much of the research, particularly in pest management, is irrelevant to the farmers' needs. Research scientists are not encouraged to work in, or even visit, farmers' fields. Research budgets are largely swallowed by salaries and equipment, so there is seldom provision for adequate local travel.

New plant types and farming systems that are developed on research stations with adequate plant protection, assured moisture and high soil fertility may well prove to be expensive failures where all of the inputs are not available to the farmer.

Agricultural research must be conducted with relevance to farmers' fields. At ICRISAT, we reserved 100 ha of our farm for pesticide free research. All new plant selections are eventually tested in this area to ensure that they are not unduly susceptible to the locally common pests and diseases. Additionally, all new varieties are tested under high and low fertility, and under moisture stress, to ensure that those with unacceptable susceptibilities do not reach the farmers. This does not imply that we have to accept the traditional low yields associated with low input farming. There is obvious potential for high yielding varieties that benefit from the increased inputs that are now being made available to farmers, as was evident in the green revolution. We have to cater for the low input farmer separately, with varieties that contain the essential resistances. The logistics of such multifaceted research involves many coordinated trials of many advanced selections of plants and would not be possible without sophisticated methodology, utilising the available germplasm, expensive scientific equipment, computers, and competent and enthusiastic teams of scientists and technicians. Individual developing countries cannot afford such research for each of their crops, so multinational efforts are essential.

It is not suggested that such multinational or regional research should replace the national research and development agencies. The IARCs regard the national scientists as the customers for their products. These national scientists have to select and adapt the products of the IARCs for the benefit of their local farmers. Local economics will determine whether inputs such as insecticides can be profitably used and the national entomologists have to calculate economic thresholds. Development and increased productivity is evident in many countries, particularly where political and economic stability allow such progress.

CONCLUSIONS

Agricultural productivity must expand rapidly to feed the increasing populations in the developing countries. Research station reports clearly show that we already have the technology to greatly increase yields from food crops and that pest caused problems can be controlled. The major question is whether it is economically feasible for farmers to exploit the available technology if the necessary inputs are made available. At this time there is little or no alternative to insecticide use in high yield farming. With the notable exception ofIndia, where 90% of the insecticides used are manufactured internally, almost all developing countries have to import most insecticides, so increasing their foreign exchange problems. Just as a good engineer is one who can make a good machine cheaper, so entomologists must be encouraged to develop cheaper means of pest management. The most promising route appears to be through host plant resistance, which is cost free once the seed is in the farmers' hands. Past progress in the exploitation of such resistance has been lamentably slow, but determined efforts in the International Agricultural Research Centres appear to be paying off. Biotechnology, particularly genetic engineering, may provide us with the means of accelerating the selection and breeding of resistant crop plants. There is scepticism about the high cost and speculative nature of "biotechnology research" but it is unlikely to be less productive than most of the pest management research that has been conducted over the past 30 years.

There is justified concern about the use of pesticides in developing countries, with the evolution of resistant pests, destruction of fauna and poisoning of people. We cannot ignore these problems and we have to react urgently to them. However, it is also evident that most pesticide use in the developing countries has been profitable and the cost of chemicals has generally prevented farmers from using them too lavishly.

Much pest management research, including that in the developing world, is fragmented and uncoordinated, with considerable duplication. The target of most publicly funded research appears to be the research journal rather than the farmers' field. While there is a need for basic and component research to provide a foundation for well planned pestmanagement, there is an even greater need to develop practicable action in farmers' fields and there is little evidence to show that this is an energetically pursued primary objective. I regret that my experience has convinced me that further developments of pest management in farmers' fields are most likely to continue to flow from commercial companies, where profits demand deeds rather than words!

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NEW DEVELOPMENTS IN INTEGRATED DISEASE MANAGEMENT IN TROPICAL PLANTATION CROPS

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ABSTRACT

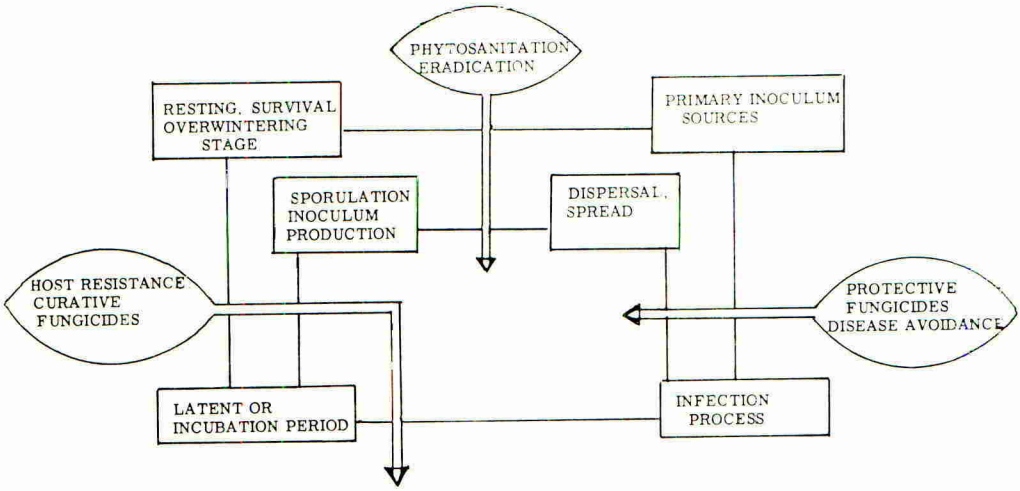
The characteristics of tropical plantation crops greatly influence the strategies for disease control. Chemical disease control methods have been more widely used on these crops than on annual crops, and the efficiency of these methods is now being improved by more effective fungicides, better application techniques and by the integration of other disease control methods. Phytosanitary methods are still the mainstay for control of soil borne root pathogens, but the integrated use of chemical and biocontrol methods are now being used. The use of host resistance for control of perennial crop diseases faces several problems including the need for durability and a long development time but effective resistance against several epidemic diseases of plant shoots and fruits is now becoming available.

INTRODUCTION

The options for disease control in agricultural crops can broadly be grouped into chemical, cultural and genetic methods. There is generally less reliance on pesticides for controlling diseases than there is for controlling arthropod pests. The principles for cultural control of diseases such as crop rotation and general methods of crop hygiene were evolved long ago and remain just as relevant today. Disease control by the selection and use of resistant cultivars has become dominant on annual crops and now protects the world's staple food crops from the ravages of most pathogens. By contrast, disease resistance is much less widely used in perennial crops and chemical control methods are more prominant particularly on some of the tropical plantation crops where export value is sufficient to carry the cost. Figure 1 shows a diagrammatic representation of a generalized pathogen life cycle and the points where particular control strategies are effective. Of particular importance is the relevance of primary source inoculum, which can often be greatly reduced by phytosanitary or hygiene methods, and of secondary inoculum produced within the crop by successive generations of infection, sporulation and dispersal. The latter produces polycyclic epidemics typical of many airborne pathogens of plant shoots. Crop species are attacked by a spectrum of diseases; different methods are used against different pathogens and there are examples of where control of one can exacerbate another, hence the need for careful integration of the methods used.

FIGURE 1

Generalized pathogen life cycle and control strategies



CHARACTERISTICS OF TROPICAL PLANTATION CROPS THAT INFLUENCE DISEASES CONTROL STRATEGIES

"Plantation" crops cover a broad spectrum of species grown for a wide range of purposes, from high value beverage tree crops to the herbaceous semi-perennials such as sugarcane and sisal. In this paper, I shall concentrate on the woody perennials such as rubber, coffee and cocoa. The term "plantation" is taken to mean a permanent planting whether organised on an estate basis or grown as smallholder plots.

The perennial nature of these crops probably has the largest influence on disease control strategies largely because host resistance is more difficult to employ than in annual crops. Not only is the breeding, selection and use of resistant cultivars a much longer process but the resistance must also be durable. This is because shifts to other cultivars possessing different resistance genes to combat changing virulences in pathogen populations cannot be as readily accomplished as it can with annual crops. The products of perennial crops are often destined for overseas markets where quality may be of prime consideration (beverage crops) or where there is a carefully planned shipping and ripening schedule (bananas) so that the influence which cultivar changes may have on these characters needs careful consideration. Sugarcane is the obvious exception here as virtually all disease problems have been successfully controlled using resistant cultivars and this resistance has proved durable. Breeding for durable resistance in perennial crops has been discussed by FAO (1986).

The size and permanence of perennial crops makes other disease control practices more difficult as well. There is little opportunity for cultural or biocontrol of soil borne diseases between seasons and the target of fungicide application is often difficult to reach and cover adequately. The long term health of the plant must be safeguarded as disease levels in one year frequently affect productivity in the subsequent years. Perennial evergreen crops growing under equatorial conditions may suffer a continuous epidemic of leaf diseases, a situation which has prevented the effective monoculture of rubber in the Amazon basin and severaly hampers cocoa growing there.

The large scale nature of estate plantation cropping including investment backing and managerial control means that intensive disease control practices involving surveying, monitoring and spraying can be more easily achieved than in other cropping situations. However, many of the higher value plantation crops are now grown by smallholders so that these characteristics no longer strictly apply and this is leading to changes in disease control practices.

Whether these crops are grown by smallholders or under estate management, they still represent a long-term investment; each individual plant has a high value both intrinsically and productively, therefore disease control practices which may be uneconomic on other crops are often worthwhile on these. Even so, economic pressures are forcing more attention to be paid to reducing the relative costs of crop protection activities, particularly as both labour costs and material costs (chemicals and fuel) have risen much faster than market prices for produce since the late 1970's.

Consideration of the disease situation affecting different parts of perennial crop plants illustrates the varied strategies used for disease control in plantation crops.

SOIL BORNE PATHOGENS

This group of pathogens are particularly significant for perennial crops because of their lethal effects and insidious spread through the soil over the years. These diseases often show a patchy distribution and even though the rate of disease spread and development may be slow, death of an increasing proportion of trees results in a reduction of the economic life of the plantation as a whole; smallholders with relatively few trees can be devastated. Overt symptoms of these diseases such as chlorosis and wilting are usually manifested when affected plants are already too badly diseased for remedial action and by this time neighbouring trees have often become infected.

Root rots

Causal pathogens of these are often Hymenomycetes with *Ganoderma* (especially on oil palm), *Rigidoporus* (especially on rubber), *Phellinus* and *Armillaria* being the main genera involved; Ascomycetes such as *Rosellinia* may be significant locally. These are non-specialized necrotrophic pathogens with wide host ranges and useful host resistance is not known.

Typically, these diseases arise from larger sources of pathogenic inoculum in the soil such as the roots and stumps of previous crops on forest trees. Because of their relatively slow spread and multiplication rate during the life of the crop, sanitation measures aimed at removing these inoculum sources have been traditionally and effectively used. These include mechanical stump and root removal, ring barking to cause root starvation before felling, etc. However, there are various contra-indications to this approach particularly cost and agronomic disadvantages. Chemical treatments to poison stumps using 245- T or sodium arsenite have been used; subsequent colonization of dead stump tissues by competitive saprophytic fungi excludes the pathogens. Nowadays the more acceptable chemical ammonium sulphamate is often used. This has been shown to have greater effect in promoting colonization by biological competitors (Turner 1982).

Stump treatments are generally applicable only before the crop is planted but disease which appears within the crop after planting also needs to be controlled and measures aimed to facilitate early detection of disease have enabled chemical treatments to be effectively used. In rubber, routine inspection for trees showing incipient symptoms, their subsequent removal, with inspection and treatment of the root bases of neighbouring trees limits disease development. The use of leguminous cover crops in rubber promotes soil surface mycelial growth of Rigidoporus enabling easier detection at stem bases before invasion occurs and acts as a 'decoy crop' in promoting mycelium growth and sporulation in the litter layer with the consequent exhaustion of inoculum bases in teh soil before trees can be infected. These cover crops also accelerate and enhance the natural biological control processes which destroy the soil borne inoculum bases of these pathogens. Such forms of indirect biological control and more direct inoculative treatments have a significant role to play in reducing costs of root disease control.

Even so, the application of more potent systemic fungicides has now enabled better integration of chemical control techniques with the time-honoured sanitary practices for controlling both the initiation of disease foci and subsequent spread within the crop. Rigidoporus on rubber has been controlled by soil application of tridemorph (Tram Van Canh, 1985) and more recently by triazoles (Anon 1987). While Ganoderma on oil palm is also controllable by soil applied triazoles (Lim & Ng, 1988).

Wilts

There are several wilt diseases of tropical plantation crops caused by soil borne pathogens particularly Fusarium and Verticillium. These are more specialized and host specific than those causing root rots, and host resistance has been found and successfully used to control many of them. For others, control is problematic as inoculum is dispersed throughout the soil and inaccessible and chemical control is not economically feasable. Current measures rely on containment.

AIR BORNE PATHOGENS

Diseases affecting the aerial parts of plants are more accessible to control measures than are root diseases, but this is more than offset by their polycyclic epidemic nature and the influence of seasonal irregularities on cropping pathogens in tropical areas.

Foliage and shoot diseases

The major foliage diseases of coffee (rust - Hemileia vastatrix), tea (blister blight - Exobasidium vexans) rubber (secondary leaf fall and South American leaf blight (SALB) - Microcyclus ulei) and cocoa (witches' broom disease - Crinipellis perniciosa) are classic polycyclic epidemic diseases which are difficult to control on evergreen tree crops under equatorial conditions. Durable host resistance is the ideal answer but is often thwarted by problems of pathogen variability.

There have been problems with "breakdown" of resistance against coffee rust but resistance derived from Catimor hybrids is holding up in Colombia where several thousand hectares have been planted since 1984. These hybrids possess grade A resistance - 5 major resistance genes covering the known 32 races of H. vastatrix. This does not guarantee durability but other resistance factors are present in these hybrids (Eskes, 1983) which may reinforce it. In rubber resistance to SALB is available from wild Hevea clones (Anon, 1985) and other Hevea species and certain clones possess resistance against some of the secondary leaf fall pathogens. Grafting resistant 'canopy' clones onto high yielding root stocks (the foliage of which may be susceptible) is enabling more rapid exploitation of host resistance.

Resistance to cocoa witches' broom in the Scavina hybrids has been shown to be ineffective against the more virulent races of the pathogen present in the Andean foothills and W. Amazon area (Wheeler, 1987) and the disease is very serious in new Amazonia plantings in Brazil. Chemical control of these diseases is often hampered by application problems especially on trees such as rubber and cocoa. Dusting and thermal fogging techniques have been used to infiltrate the canopies of mature rubber trees but high pressure hydraulic hand lances are most frequently used for application to tree crops. On shorter crops such as tea and coffee more refined techniques are possible. For control of coffee rust in mountainous, often isolated areas, conventional spraying techniques are difficult to use and impose severe constraints on small farmer productivity. Portable ULV techniques can provide suitable answers and will permit more efficient and timely applications with less inputs in terms of materials and labour enabling the small farmer to divert these scarce and expensive resources to other enterprises (Fernandez et al, 1986). Recent work in Colombia using air assisted ULV techniques have shown that placement of fungicide deposits directly beneath coffee leaf surfaces where rust infection occurs is possible throughout the dense canopies of Caturra coffee. Bioassay techniques applied to droplet density and concentration tests of a flowable copper oxychloride formulation indicate that the theoretic minimum dosage is in the order of 20 ng/cm^2 leaf area - equivalent to about 20 gm/ha. For field control this dose would need to be greatly increased to allow for persistence and redistribution but it still serves to indicate the magnitude of the gap between the actual and the attainable.

New and more efficient fungicides are also producing significant benefits on control of leaf diseases. Some triazoles are particularly effective at low doses against coffee leaf rust (Shephard, et al, 1986) and against SALB of rubber (Santos & Pereira, 1986). The potency and systemic nature of these compounds can enable novel application methods to be used.

The efficiency of chemical control depends greatly upon the correct timing of spray applications. This is dependent upon a knowledge of disease epidemiology, crop growth patterns and the climatic parameters which influence them. Disease forecasting techniques can be built up which allow further refining of spray application and such techniques are currently being evaluated in Brazil (Kushalappa, et al, 1986).

Phytosanitary measures to reduce initial inoculum have little effect on the subsequent development of most of the polycyclic diseases. Attempts to contain or eradicate outbreaks by these methods have met with only limited success (Waller, 1979; Thresh and Owusu, 1985). However, where the susceptible stage of the crop is restricted or where there is some spacio-temporal separation from the inoculum source, then these methods can be effective. It has long been recognized that cocoa witches' broom disease can be controlled in some areas by phytosanitary measures to remove old brooms and other sources of inoculum at the end of the season. A knowledge of the epidemiology of the disease has enabled factors which favour disease development to be identified. Various agronomic practices such as untimely pruning, fertilizing, lack of shade, the use of self incompatible hybrids leads to the prolongation of vegetative flushes and flowering thus extending the susceptible phases of the crop and exacerbating the epidemic (Evans, 1981). Measures designed to reduce this, coupled with dry season pruning and fungicidal protection of developing pods to reduce the important pod rot phase can now give adequate control.

Fruit diseases

These are particularly significant on cocoa where a range of pod diseases require control and have been estimated to cause loss of produce theoretically valued at £1,500 million per annum (Evans & Prior, 1987). On coffee, coffee berry disease (CBD) caused by Colletotrichum coffeanum still causes control problems in parts of Africa.

Resistance to CBD has been known to exist in several varieties for some time and appears to be durable, but it has only very recently been incorporated into cultivars with high yield and quality characteristics The high quality coffees of many African countries are susceptible to the disease and chemical control is required. The effectiveness of resistance to cocoa black pod is complicated by the involvement of several different Phytophthora species (4 in Brazil) which have varying host/pathogen relationships; resistance to one species is not always associated with resistance to the others. Nevertheless, good general resistance has been detected in some clones.

Control of cocoa black pod and of CBD by fungicide application to developing fruits is essential in countries where these diseases are damaging. Problems centre around the need to protect expanding fruit surfaces during wet tropical weather and the difficulties of fungicide placement on the target (Mabbett, 1986). Both black pod and CBD are wet weather diseases, the pathogens being primarily water dispersed and fungicide redistribution plays a major role in the efficacy of their chemical control. Not only can fungicide redistribution in rain water from a deposited reservoir within the tree canopy be available for protecting expanding fruit surfaces, but water which disperses the pathogen will carry fungicide with it. Unfortunately, this secondary

protection is of variable efficacy and requires relatively large doses of fungicide applied throughout the canopy (to provide a reservoir above the crop). Under very wet conditions and with heavy inoculum pressure, control may not prove adequate. Nevertheless for control of cocoa black pod Pereira (1985) has shown that in Bahia (Brazil), the most cost effective treatment is the application of a few widely spaced heavy doses of copper fungicide using high volume 3-400 1/ha (60-70% more cost effective than mist blowers applying low doses and volumes more frequently).

Copper fungicides are still widely used for black pod control; a synergistic effect of mixing in a small quantity (10%) of fentin acetate has allowed doses to be reduced in Brazil, where the omission of stickers was also found to give better control, probably through improved redistribution (Pereira, 1985). Systemic fungicides such as metalaxyl have proved effective against black pod and a metalaxyl and copper mixture has been recommended in PNG (McGregor, 1983). Most recently, it has been shown that trunk injections of a commercial preparation of phosphonic acid will control Phytophthora diseases of rubber and avocado (Lim, et al 1988).

Captafol has been the most effective chemical for CBD control for many years in Kenya but it is less effective against coffee rust and exacerbates bacterial blight (Pseudomonas syringae). Consequently chemical control of these diseases has to be integrated using different spraying schedules and fungicide mixtures according to season and locality (Kairu, 1985). There is a need now for an effective fungicide to replace captafol.

A knowledge of the epidemiology of fruit diseases has enabled the exploitation of some measures which can improve the efficiency of chemical control when integrated with it. Spacial or temporal separation of inoculum sources from susceptible stages of the crop form the basis of these and foremost among them, is the control of cropping patterns. Diseased fruit and other inoculum sources carried over from previous or overlapping crops are a potent source of pathogen inoculum to initiate rapidly progressing seasonal epidemics; the prevention of overlapping crops and removal of inoculum sources between crops has been shown to be particularly effective for improving control of cocoa pod diseases in seasonal climates. Moniliophthora pod rot and the pod rot stage of witches' broom (Crinipellis perniciosa) of cocoa in S. America is particularly amenable to this, but the variable inoculum sources for Phytophthora pod rot make this approach less effective in many equatorial areas. Conversely agronomic practices which promote continuous cropping exacerbate the condition; dry season irrigation of coffee makes CBD control particularly difficult for this reason. Timing of spray application in relation to stage of crop development and climatic factors is particularly critical for CBD control.

CONCLUSIONS

Because of the nature of perennial crops, new disease control techniques often have a long lag phase before they are adopted for general use. This applies particularly to disease resistant cultivars; only now is this beginning to be deployed against the major leaf pathogens, but it will greatly benefit the expanding smallholder sector where control measures requiring continuing inputs are difficult to ensure.

The adoption of cultural practices which disrupt pathogen life cycles can significantly improve disease control, and improved knowledge of the epidemiology of diseases affecting tropical perennial crops has enabled these to be identified. Inoculum reduction by direct phyto-sanitation or by indirect biocontrol are especially relevant to soil borne pathogens.

Developments in chemical control strategies are most significant and include the use of more effective compounds and improved spray application systems. Better understanding of disease epidemiology has led to improved timing and the integration of cultural practices to facilitate inoculum reduction. Lower doses and more critical application create less environmental disturbance and associated problems, but cost effectiveness is the main criterion for uptake by the farming community.

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SESSION 4B

THE FATE OF PESTICIDES IN THE ENVIRONMENT – RESULTS

CHAIRMAN DR S. OTTO

SESSION ORGANISER DR J. P. LEAHEY

INVITED PAPERS 4B-1 to 4B-5

ASSESSMENT OF THE IMPACT OF PP321 ON AQUATIC ECOSYSTEMS USING TENTH-ACRE EXPERIMENTAL PONDS

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ABSTRACT

Sixteen ponds, each 0.1 acre (0.04 ha) were constructed in North Carolina, USA. These were used to evaluate the potential impact of the pyrethroid insecticide PP321 on aquatic ecosytems. Sets of four replicates were treated with three rates of PP321 and controls. The insecticide was applied directly to the whole pond surface, as simulated "spray-drift" and "run-off". Residues in the water declined rapidly after application. A wide range of physicochemical and biological parameters were studied over a six-month period. It was concluded that PP321, when used as recommended for agricultural purposes, is unlikely to cause adverse effects on populations or productivity in aquatic ecosystems.

INTRODUCTION

Under laboratory conditions, in water without particulate matter, pyrethroid insecticides have a high toxicity to some aquatic invertebrates and to fish.

The pyrethroids are of very low water solubility/high lipophilicity, and therefore are rapidly and strongly adsorbed to particulate material, and associated with dissolved organic carbon. In the adsorbed state their bioavailability to aquatic organisms is greatly reduced. Consequently, under field conditions the aquatic impact of the pyrethroid PP321 is likely to be much less than might be predicted by laboratory acute or chronic toxicity test data.

Twelve ponds, each 0.084 ha in surface area, were constructed in North Carolina, USA in 1985 and were shown to be similar in water quality and biology. These ponds were divided in early 1986 to give twenty-four replicate ponds. Sixteen of the ponds were used in 1986 to assess, in a replicated study, the potential impact of the pyrethroid insecticide PP321 on aquatic organisms following simulated "run-off" and "spray-drift" applications.

This paper describes the physicochemical characteristics of the ponds and the biology of the various trophic levels in the ponds before and following multiple applications of PP321 as simulated "spray-drift" and "run-off" events in 1986. The PP321 residues in the ponds are also described.

METHODS AND MATERIALS

Pond Construction

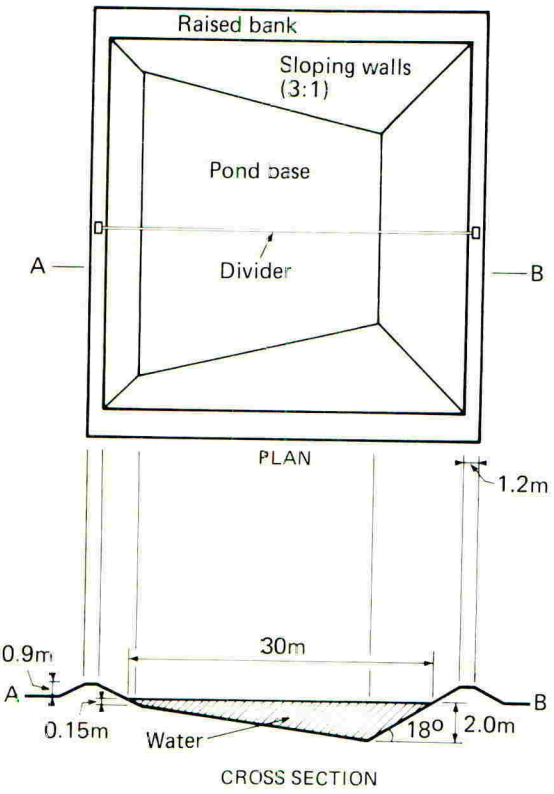
Twelve ponds, each 30m x 30m (0.084ha, 0.2ac), were excavated during 1985 at the ICI Americas Eastern Research Centre, Goldsboro, North Carolina, USA. The ponds were designed to have a water depth ranging from 15cm at the shallow end to 2m at the deepest point (Figure 1). Each pond was lined with a 15cm layer of clay covered with a 10cm layer of sandy loam soil. A 50cm high bank surrounded each pond to prevent cross-contamination between ponds and run-off entry from the surrounding land.

The twelve ponds were each longitudinally divided into two in early 1986, creating ponds 15m x 30m (0.04 ha) with a volume of 450m^3. This was accomplished using a terylene (Hypalon^{TM}) barrier with an inverted T-joint sealed into the pond hydrosoil.

A water-circulation system was installed so that the water from all ponds could be continuously mixed in the period before pesticide application. Overflow pipes for each 0.04 ha pond led to a pumping chamber, from where water was returned in parallel to all twenty-four ponds. The chamber had a well-water inlet so that the ponds could be "topped-up" when evaporation substantially exceeded rainfall.

Sixteen of these ponds were used to evaluate the potential impact of PP321 on aquatic ecosystems.

Figure 1 Pond design

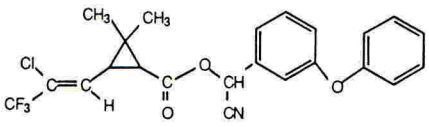


Biological Establishment of Ponds

The experimental ponds were initially filled with water from a large, adjacent natural pond with substantial and diverse populations of aquatic organisms. In addition, macroinvertebrates collected from several local ponds were also added to the experimental ponds.

An aquatic macrophyte, Ludwigia, was planted in 1985 in the shallow region and around the perimeter of each pond. The central area of each pond was left free of macrophytes to facilitate sampling procedures.

PP321, proposed common name lambdacyhalothrin, is a racemic mixture of the enantiomers (S)-α-cyano-3-phenoxybenzyl (1R)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (R)-α-cyano-3-phenoxybenzyl (1S)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylclopropanecarboxylate, designated enantiomer pair B.



The possible enantiomer pairs are A-D and A′-D′. Enantiomers A′-D′ have an E configuration; the A and B isomers have a cis-configuration about the cyclopropane ring and the C and D isomers a trans-configuration.

The ponds were treated with Karate™, an emulsifiable concentrate (EC) formulation of PP321 (13.8% ai w/w; containing >98% enantiomer pair B).

Application of PP321 to Ponds

The application programme began in early June 1986. Three rates of PP321 were applied, with four replicates for each rate. Four ponds were left as controls.

Twelve "spray-drift" entry applications were made to each pond by spraying evenly over the whole pond surface at weekly intervals. The rates used were 0.017, 0.17 and 1.7gai/ha (to the low, medium and high rate ponds), equivalent to 0.05, 0.5 and 5% of the maximum recommended field application rate for cotton. Six "run-off" entry applications were also made to the same ponds, one application every two weeks. "Run-off" treatments were applied as soil-water slurries (250kg soil and 2500 litres water) sprayed evenly onto the whole pond surface. The rates were 0.05, 0.5 and 5gai/ha (to the low, medium and high rate ponds). Soil-water slurries without PP321 were also applied to the control ponds.

Each PP321 application to the medium rate ponds was calculated to give the maximum expected environmental concentration (MEEC). Therefore the total programme of 18 applications to these medium rate ponds resulted in a much greater exposure of aquatic organisms to PP321 than will occur following agricultural use.

"Spray-drift" and "run-off" applications were made with a travelling spray-boom which spanned the entire 15 metre pond width.

Pond Sampling

The majority of sampling techniques, biological observations and direct physicochemical measurements were carried out within two zones in each pond. The shallow-zone had an average depth of 50cm and the deep-zone was up to 2 metres deep.

The ponds were studied from September to November 1985 to examine numbers of organisms, species diversity, productivity and pond-to-pond uniformity, in order to determine their suitability for the pesticide study during 1986. As they were found satisfactory the programme proceeded.

The 1986 schedule involved sampling prior to the first PP321 application, sampling at 2 week intervals during the 12 week application period, and then every 2 - 3 weeks during the 3 months after the final treatment. Throughout the application period, pond visual observations of the pond for effects of the pesticide were also made several times each week, and the emergence traps were emptied twice per week. Replicate samples collected in a zone and at each interval were composited for analysis, although surface and bottom harvests of invertebrates were kept separate.

Phytoplankton and Zooplankton

Water samples were collected as vertical, integrated cores and preserved for analysis of cell number and identification, and for phytoplankton cell volumes and photosynthetic pigments. Photosynthesis and respiration were also measured *in situ* using light and dark bottles, and total community metabolism was calculated from "dusk-dawn-dusk" dissolved oxygen determinations.

Periphyton

Integrated depth samples of periphyton were harvested from plastic strands hung vertically through the water column. The substrates were removed from the ponds after 7 - 14 days colonisation and periphyton analysed for cell number, identification, cell volume and photosynthetic pigments. Total biomass was also determined to enable calculation of the autotrophic index.

Macroinvertebrates

The macroinvertebrate populations were studied using artificial substrates, insect emergence traps and by direct observations of the ponds. The organisms on the substrates were transferred directly to trays for counting and identification, whereas the emergence trap samples were initially preserved.

Fish

Observations of fish in quadrats were made throughout the study period. All the fish were harvested in early November 1986 by Seine-netting, and then fully draining down the pond followed by manual collection. The fish were size grouped, counted and weighed.

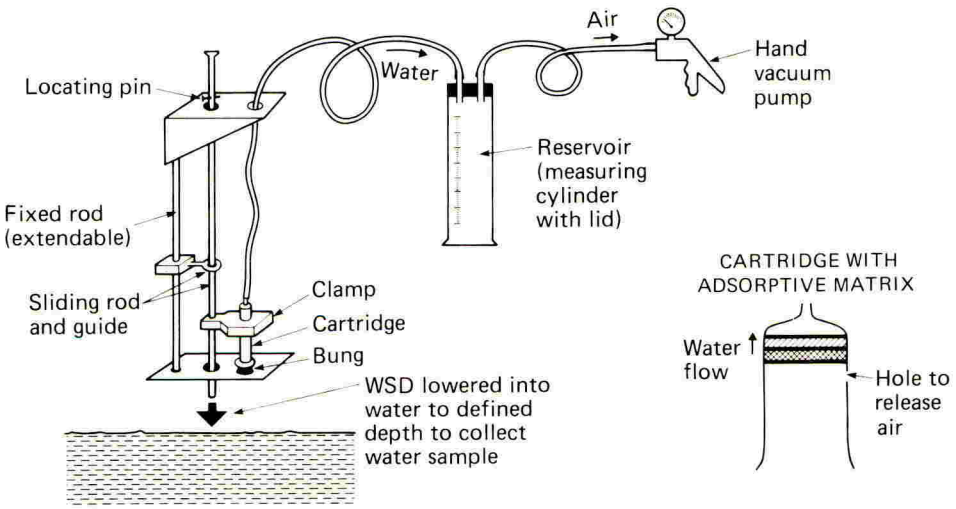
Physicochemical Characteristics

At the start and end of the 1986 study period, the pond water and hydrosoil were analysed for a wide range of both pesticides and physicochemical parameters. At each sampling interval pond water was analysed in situ for pH, temperature, dissolved oxygen and conductivity, and in the laboratory for turbidity and alkalinity.

Pyrethroid Residues

Pond water was sampled in the two zones and from both near the surface and close to the hydrosoil. Residues were collected using an adsorptive-matrix technique, with the adsorbent packed in a cartridge. Activated cartridges were held in a sampling device (Figure 2), which enabled each cartridge to be opened at a defined depth and a prescribed volume of pond water to be passed through the adsorbent.

Figure 2 Water sampling device (WSD)



Analysis of the pyrethroid residues was carried out by fortifying the adsorbent with an internal standard followed by solvent elution, clean-up and capillary GLC using electron capture detection. PP321 (B enantiomer pair) was resolved from its epimer, the A enantiomer pair, and from any of the other isomers. The limit of determination (LOD) for each enantiomer pair was set at 1 ng/l pond water. Mass spectrometry was used to confirm residues in a representative number of analyses.

Hydrosoil was collected by a coring technique, from both the shallow and deep pond zones. The cores were cut into 2.5cm or 5cm depth fractions whilst frozen. Analysis was by organic solvent reflux extraction, clean-up and GLC with either electron capture or mass spectrometric detection as described for water analysis. The LOD for each enantiomer pair was 0.2 µg/kg dry weight hydrosoil.

RESULTS

Biology and Physicochemical Characteristics

Prior to the application of PP321, all the ponds contained substantial and diverse populations of aquatic organisms and pond-to-pond comparability was good. A summary of the overall biological and physicochemical results is given for the study period in Table 1, and representative data for selected groups of organisms are shown in Figures 3 - 6.

Table 1 : Effects of PP321 Applied at Three Rates to Pond Ecosystems

Parameter	Low rate	Medium rate	High rate
Physicochemical	-	-	-
Microbial (hydrosoil)	-	-	-
Phytoplankton & Periphyton			
cell numbers, volume, biomass	-	-	-
taxonomic groups	-	-	-
activity	-	-	-
Filamentous algae	-	-	-
Macrophytes			
Zooplankton			
Protozoa	-	-	-
Rotifera	-	-	-
Crustacea	-	-	++(r)
Macroinvertebrates			
Turbellaria	-	-	-
Mollusca	-	-	-
Oligochaeta	-	-	-
Hydracarina	-	+(-)	++(-)
Ephemeroptera - Baetidae	+(R)	++(r)	++(r)
- Caenidae	-	++(r)	++(r)
Odonata - Anisoptera	-	-	-
- Zygoptera	-	-	+r
Hemiptera - Belostomatidae	-	-	++(-)
- Gerridae	-	++(r)	++(nr)
- Notonectidae	-	-	++(-)
- Veliidae	-	++(-)	++(-)
Coleoptera - Hydrophilidae	-	-	-
- Haliplidae	-	-	++(-)
Trichoptera - Leptoceridae	-	+(R)	++(nr)
Diptera - Ceratopogonidae	-	-	+(R)
- Chironominae	-	-	-
- Tanypodinae	-	+(R)	++(r)
Fish (Lepomis macrochirus)			
activity	-	-	-
numbers and weight	-	-	-

- = no effect; + = minor effect; ++ = major effect; (R) = full recovery by study end; (r) = partial recovery; (nr) = no recovery; (-) = not possible to judge recovery.

The multiple applications of PP321 had no effect on any of the physicochemical parameters measured.

The numbers and activity of planktonic and periphytic algae, the filamentous algae and the macrophyte biomass were all unaffected by the applications of PP321 even at the high rate. The total zooplankton population showed no overall effect from PP321. The highest rate of application of the insecticide did however reduce numbers of crustaceans.

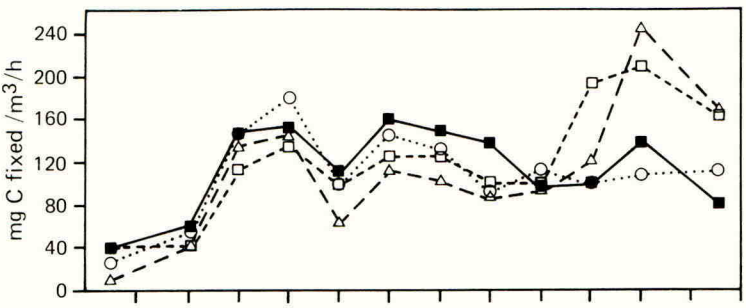


Figure 3a
Planktonic gross productivity from light and dark bottles

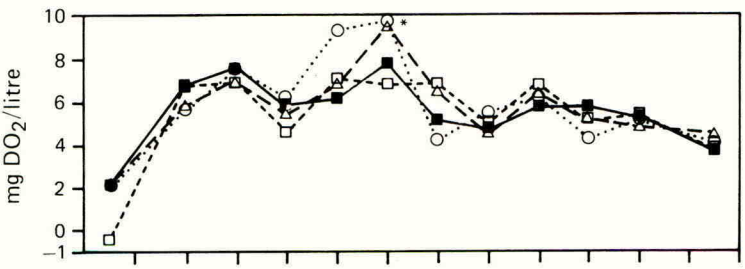


Figure 3b
Total community photosynthesis from dusk—dawn—dusk dissolved oxygen measurements

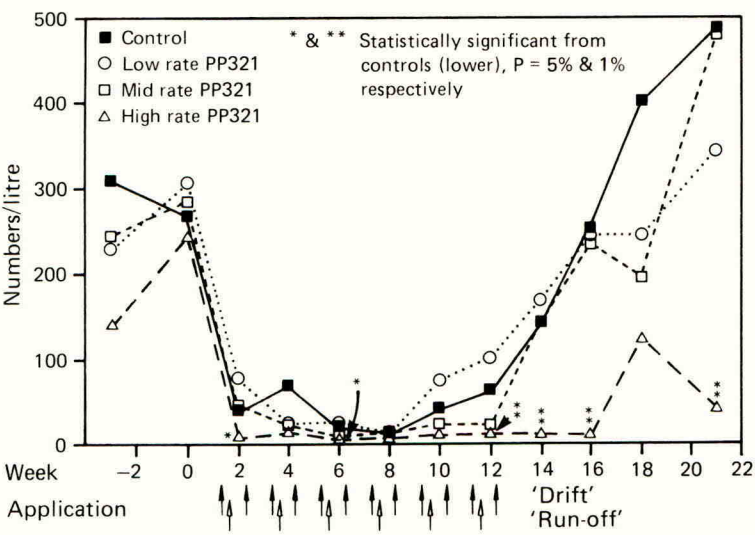


Figure 4
Planktonic crustacea

Some of the macroinvertebrate groups were substantially affected by the high rate of PP321. However, at the medium rate few effects were apparent and at the low rate virtually none occurred. The organisms most affected were Ephemeroptera and Zygoptera nymphs, Notonectidae, Veliidae and Chironomidae (Tanypodinae). Molluscs were unaffected at all rates, as were those groups of organsims living within the hydrosoil (Oligochaetae and Chironomidae [Chironominae]). There was a general decline in treated and control ponds in the density of some macroinvertebrate groups in June, probably resulting from fish predation. Baetidae and Zygoptera nymphs, Leptoceridae larvae, Notonectidae, Dytiscidae and Chironomidae (Tanypodinae) were reduced in this manner.

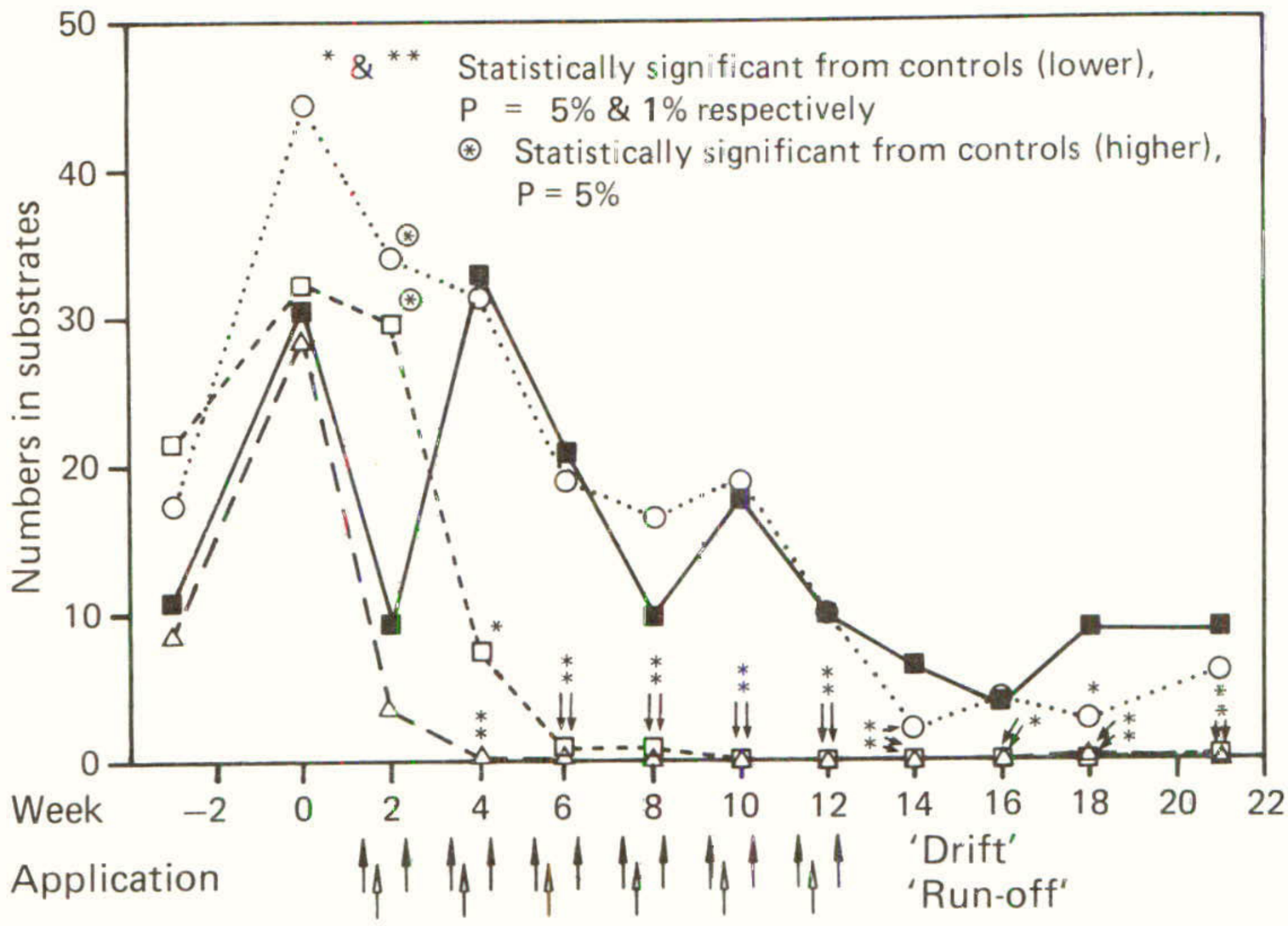


Figure 5
Ephemeroptera Caenidae Nymphs

PP321 had no effect on the bluegill sunfish populations at any application rate. Approximately 300,000 fish were harvested from the 16 ponds at the end of the study. In individual ponds numbers ranged from 14,000 to 22,000 fish and total weights were between 7 and 14 kg. Tadpoles were harvested with the fish, with an average weight of 3-4 g per tadpole. Numbers were very variable and not treatment related.

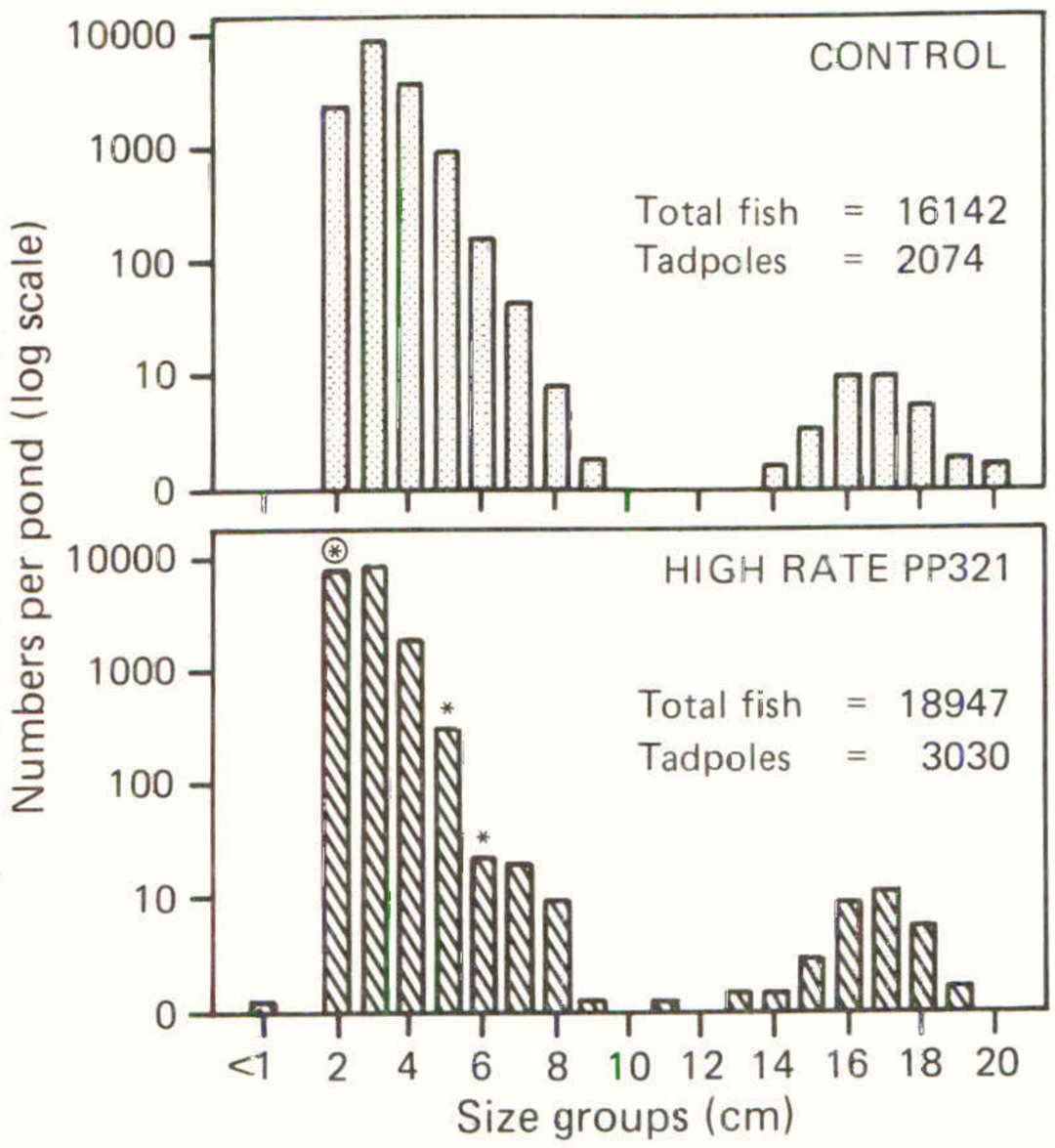


Figure 6
Bluegill sunfish populations at study termination

Pyrethroid Residues in Pond Water and Hydrosoil

The residues in pond water from two of the high rate ponds are shown in Figure 7. Residues in medium rate ponds were near the limit of determination and therefore low rate samples were not analysed. The residues were comprised of the enantiomer pairs B and A in a ratio of approximately 1:1 on all occasions. All the other isomers were below the LOD. PP321 (isomer B) has been shown in the laboratory to epimerise to the enantiomer pair A in water at pH values above 7, whereas aqueous photolysis results in the additional formation of the trans isomers C and D. The formation of only isomer A in the ponds is not surprising as the water pH was in the range 7-9, and because photolytic processes are rarely of significance under these conditions, due to the high attenuation of sunlight in natural waters.

Residues in the water were measured 3 days after each "run-off" application. Total pyrethroid (isomers B and A) residues increased from approximately 5 ng/l to about 20 ng/l over the six applications. Where residues were measured both 1 and 3 days after spraying, the water residues declined by around 85% over the 2 day period. During the post-treatment period, pyrethroid residues fell to about 1-2 ng/l. It is likely that these residues were adsorbed to hydrosoil particles disturbed by fish activity.

The hydrosoil residues from the high rate pond are illustrated in Figure 8. Again, residues in medium rate ponds were near the limit of determination and low rate samples were not analysed. As with the water there was conversion to isomer A, with a B:A ratio generally about 2:1. During the application period total pyrethroid residues in the hydrosoil increased from 6 µg/kg dry weight during week 1 to 30-40 µg/kg in week 12. In the post-spraying period no further increase was shown and there was an indication that the residues were declining. The residues principally remained in the top 2.5 cm of the hydrosoil cores, but with time, residues in the 2.5 - 5cm depth fraction increased to approximately 20% of the total recovered pyrethroid residue.

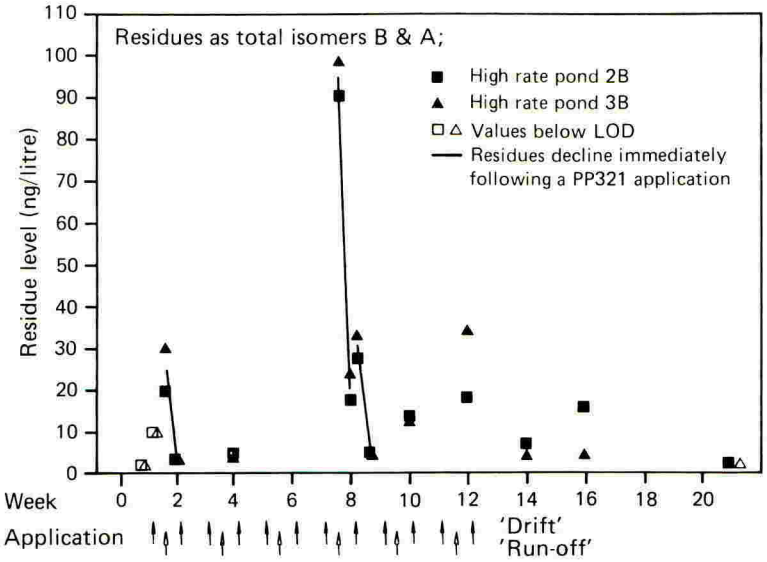


Figure 7
Residues of PP321 in water from high rate ponds

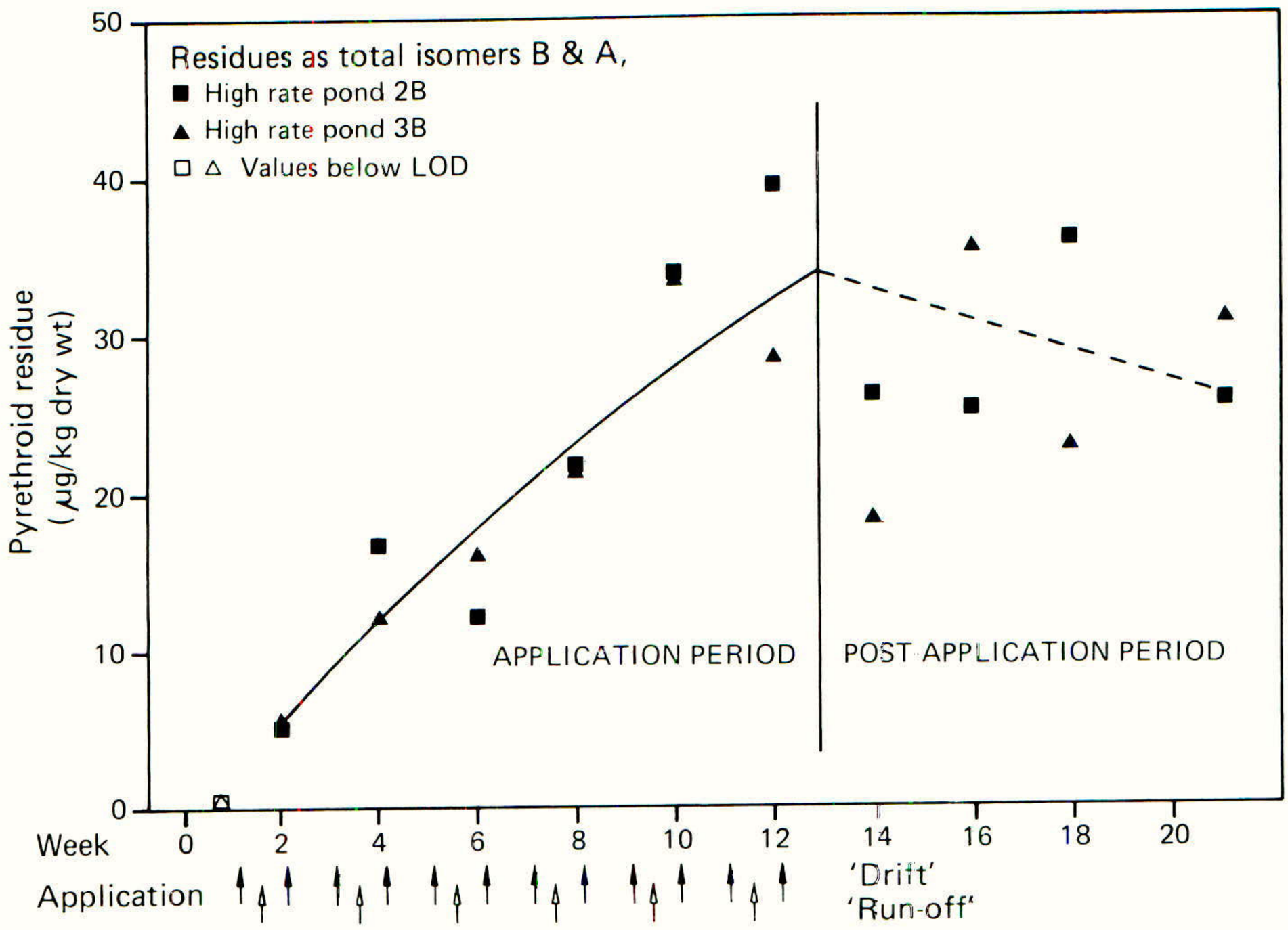


Figure 8 Residues of PP321 in hydrosoil from high rate ponds

CONCLUSIONS

Throughout the application period the total residues of PP321 in the pond accounted for between 20 and 40% of that applied; the remainder possibly being adsorbed onto filamentous algae and macrophytes, which were not sampled. The rapid fall in residue concentrations in the water, after spraying, was probably due to adsorption of PP321 onto plant material and bottom sediment, while with increasing time, it is probable that degradative processes were also contributing.

The overall biological effects observed at application rates representing worst case "expected environmental concentration" were minor and transient, and compatible with extrapolations from laboratory sediment-water toxicity tests. Zooplankton, phytoplankton, periphyton, filamentous algae, and macrophytes were all unaffected. Numbers of some macroinvertebrates, such as the Ephemeroptera nymphs, the Chironomidae:Tanypodinae and the surface dwelling Notonectidae and Veliidae, were reduced. PP321 had no effect on fish populations.

ACKNOWLEDGEMENTS

We are grateful to the many people who have contributed to this study; especially to J F H Cole, J K Sadler, E Bolygo, D J Tyldesley, G Cullen, P D Francis, M Moore, E Farrelly, M J Hamer, J L Neal, W Cody, V Kennedy, D L Castle and P D Askew.

RESULTS AND IMPLICATIONS FROM MONITORING GERMAN RAW WATER FOR RESIDUES OF A WIDE RANGE OF PESTICIDES

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ABSTRACT

On 15.7.1980, a controversial single maximum acceptable concentration (MAC) was laid down for all pesticides in the EEC Directive (80/778/EEC) on "the quality of water intended for human consumption". This directive stimulated the German Pesticide Trade Association (IPS) to carry out, in 1985/1986, a monitoring programme of pesticide residues in raw water (mainly from ground water sources) in order to obtain information on the occurrence and levels of contamination of raw water with pesticides. The study also addressed the issue of problems encountered in ultra-trace analysis. Raw water samples were taken at several time intervals from 206 waterwork wells across the FRG. Analysis for 35 pesticide active ingredients (a.i.) was carried out. Seven of these, atrazine, bentazone, chloridazon, CMPP, 1,2-dichloropropane, pyridate and simazine were found in excess of the EEC MAC of 0.1 µg/l. However, in a number of cases these findings were isolated single values. Dinoseb-acetate, 2,4-DP, isoproturon, pendimethalin and vinclozolin were detected at concentrations between 0.05 µg/l (LOD) and 0.1 µg/l. The implications of these results are discussed.

INTRODUCTION

The detection of some crop protection chemicals (pesticides) at trace levels in water (i.e. ground water, surface water and drinking water) has quickly become one of the most important issues facing agriculture, the public and the agricultural chemicals industry today. It is a multi-faceted, complex issue involving many scientific and technical disciplines such as geology and hydrogeology, soil chemistry, analytical chemistry, physical-chemical properties of crop protection chemicals, toxicology, agronomic practices, agricultural management practices, and also environmental factors such as climate, sunlight and rainfall. In addition, it is a highly controversial and emotional issue pitting the interests of those who regard an "unburdened" environment *per se* as of utmost importance against those of agriculture who seek to maintain the supply of adequate food and fibre production at a reasonable cost.

In the European context, the issue of pesticides in water has reached a particularly problematic level as a consequence of the EEC Directive (EEC/80/778) On The Quality of Water Intended For Human Consumption, which stipulates a maximum admissable concentration (MAC) of 0.1 µg/l and 0.5 µg/l for an individual pesticide and the total of all pesticides present, respectively.

These limits were obviously not set against potential hazard arising from the consumption of drinking water contaminated with pesticide residues, because a single value cannot reflect the enormous differences in toxicity and thus potential hazard of pesticides. It appears that the level of 0.1 µg/l agreed in the late 1970's was set arbitrarily at the limit of determination achieved for some relatively easy to analyse organochlorine compounds during a water monitoring programme carried out at that time. No consideration was given to analytical problems likely to arise with other types of pesticides. The level thus constitutes a zero level or quasi-zero level, which is dependent on analytical ability rather than related to potential hazard.

Confusion and concern have resulted from the public's lack of understanding of the health significance of the detection of pesticides in drinking water resources. This confusion and concern has been fuelled by the public's perception that the limits of contamination in drinking water set in the EEC Directive are "danger" levels.

As a contribution to achieving a rational debate on pesticides and drinking water in Germany, the German Pesticide Industry Association (IPS : Industrieverband Pflanzenschutz, now known as IVA : Industrieverband Agrar) decided in 1984 to carry out a large scale programme to investigate the problems that were likely to arise from the MAC setting for pesticides in Directive 80/778/EEC. Answers to the following questions were sought :

1. Is it possible to develop analytical methods for all registered pesticides, which allow the accurate monitoring of the MAC of 0.1 µg/l?

2. Are these analytical methods, with limits of determinations below the MAC of 0.1 µg/l, adequate and sufficiently robust to be used routinely for the purpose of monitoring water quality?

3. If residues of pesticides occur in raw water, what are the levels to be expected?

4. Under what geological, hydrogeological, meteorological and agronomic conditions is there a danger that traces of pesticides reach the ground water?

This paper deals primarily with the results obtained to question 3 and their implications. Questions 1, 2 and 4 are addressed in detail elsewhere (Iwan, 1988; IPS, 1987).

CONCEPT AND METHODOLOGY

The programme was conceived as a monitoring exercise of pesticides determined in samples taken directly from raw water extraction plants in seven states (Lander) of the Federal Republic of Germany (Baden-Wurttemberg, Bayern, Hessen, Niedersachsen, Nordrhein-Westfalen, Rheinland-Pfalz and Schleswig-Holstein). Raw water samples were collected for 12 to 18 months at up to 12 intervals.

Compound selection

The selection of pesticides to be included in the programme was based on one or more of the following criteria. The active ingredients should have a clear potential to be mobile and/or be sufficiently stable and/or be

important for use in German agriculture either in relation to the total quantity applied or the areas treated. Using these criteria 35 active ingredients were selected (Table 1).

TABLE 1

Active ingredients selected for the raw water monitoring programme.

	Active Ingredient		Active Ingredient
1	aminotriazole	19	isoproturon
2	atrazine	20	lindane
3	azinphos-ethyl	21	MCPA
4	azinphos-methyl	22	metamitron
5	bentazone	23	metazachlor
6	bitertanole	24	methabenzthiazuron
7	carbofuran	25	methamidophos
8	chloridazon	26	methylisothiocyanate
9	CMPP	27	oxydemeton-methyl
10	cyanazine	28	parathion
11	2,4-D	29	pendimethalin
12	2,4-DP	30	phenmedipham
13	desmedipham	31	pyridate
14	demeton-5-methyl sulphone	32	simazine
15	1,2-dichlorpropane	33	triadimefon
16	1,3-dichlorpropene	34	triadimenol
17	dinoseb acetate	35	vinclozolin
18	fluazifop-butyl		

Analytical methods

The sensitivity of existing analytical method supplied to the German regulatory authority (BBA) and used for enforcement purposes of maximum residue limit had to be improved substantially in order to achieve quantitative measurement down to the EEC MAC of 0.1 µg/l. In most cases the sensitivity of existing methods had to be improved by a factor of 100 to comply with the limit of determination of 0.05 µg/l set for the programme.

Raw water sampling site selection

In cooperation with the water industry 206 raw water sampling sites (wells) out of a total of 3771 raw water extraction plants in the Federal Republic of Germany (FRG) were selected for the programme. The individual wells were chosen on the basis that they were located in arable areas, in which the 35 active ingredients selected were mainly used. In addition, the wells should draw the water from a relatively shallow level (less than 20 m) wherever possible and be situated in geological formations which allow a high degree of penetration of water.

As can be seen from the well selection criteria used, the 206 wells included in the study were not chosen randomly and are not necessarily typical of the situation in all areas of the FRG. Thus, the monitoring

programme, in statistical terms, cannot be regarded as a representative investigation of the situation for the whole of the FRG. Primarily for reasons of capacity the monitoring programme was not planned to be such a study, but an investigation, which concentrated on certain problem areas and entailed a "worst-case" search strategy as far as well selection was concerned.

Analysis

A total of 1534 samples were taken between July 1985 and December 1986 from the 206 wells. On average, each well sample was analysed for 14 different active ingredients. Usually, the analyses were carried in the analytical laboratories of the participating companies (BASF, Bayer, Celamerck, Ciba-Geigy, Hoechst, ICI, Schering and Shell).

Details on the experiences with analysis of pesticides at ultra-trace level can be found elsewhere (IPS, 1987).

RESULTS

Overall results

The results of the raw water monitoring programme are summarised as follows and details are given in Table 2 :

- 88 of a total of 12674 analytical results were between the limit of determination of 0.05 µg/l and the EEC MAC of 0.1 µg/l.
- 54 values exceeded 0.1 µg/l with the highest value measured amounting to 5.1 µg/l for 1,2-dichloropropane.
- The values measured above 0.1 µg/l extend to 20 of the 206 wells.
- Seven of the 35 active ingredients investigated were found in concentrations above 0.1 µg/l. These are atrazine, bentazone, chloridazon, CMPP, 1,2-dichloropropane, pyridate (CL 9673) and simazine.
- Dinoseb-acetate, 2,4-D, isoproturon, pendimethalin and vinclozolin were found at concentrations between 0.05 µg/l and 0.1 µg/l.

When considering the results a number of points need to be borne in mind. It is important to remember that the determination of a substance in the concentration range of 0.05 to 0.1 µg/l is less reliable than above 0.1 µg/l, since the reliability of analytical results decreases when approaching the limit of determination. Furthermore, in a number of cases positive results were only obtained at a single sampling interval rather than seen over a period of time. At ultra-trace concentrations such as discussed in this context, a single result cannot be regarded as confirmation of contamination of a well with pesticides, but needs to be supported by a series of positive results obtained over time (Iwan, 1988).

Three further active ingredients (desmedipham, phenmedipham and metazachlor) were also found in raw water samples, but their occurrence could not be positively confirmed because of unspecific analytical methods. They have therefore been omitted from the analysis of the results. Their

measurement by determining the relevant aniline component led initially to the suspicion that they might occur in the raw water. However, with regard to desmedipham the findings had to be false positives because the compound has never been used in FRG and was only included in the programme to test the reliability of unspecific analytical methods at ultra-trace concentrations. In the case of metazachlor re-analysis with a new and specific method did not produce any positive result, thus confirming the initial measurements as false positives. The same is expected to be the case for phenmedipham.

These examples clearly indicate the problems encountered with analysis below the ppb level. They underline the necessity, to confirm apparently positive results with other specific methods and techniques.

TABLE 2

Summary of raw water monitoring programme

State	Wells	Samplings	Number of a.i. analysed	Water analyses	Analytical results above EEC MAC of 0.1 µg/l		
					Wells	Water analyses	a.i. found
					No.	No.	No.
Baden-Wurttemb.	65	403	32	5308	6	12	2 atrazine bentazone
Bayern	21	126	20	739	5	10	4 atrazine bentazone chloridazon simazine
Hessen	10	98	17	438	0	0	0
Nordrh.-Westfalen	45	404	19	1617	3	1	1 bentazone
Niedersachsen	38	209	28	3382	1	3	1 pyridate
Rheinl.-Pfalz	5	58	12	286	1	4	2 bentazone CMPP
Schlesw.-Holstein	22	236	13	904	4	24	1 dichloropropane
Total	206	1534		12674	20	54	

Individual results of compounds found above 0.1 µg/l

Full details of all results have been reported elsewhere (IPS, 1987), positive results for individual compounds are summarised in Table 3.

TABLE 3

The occurrence of atrazine, bentazone, pyridate, chloridazon, CMPP, 1,2-dichloropropane and simazine above EEC MAC of 0.1 µg/l.

Compound	State	Number of Wells sampled	Wells with Residues >0.1 µg/l	Water Samples Analysed	Water Samples with Residues >0.1 µg/l
Atrazine	Baden-Wurttemb.	14	4	98	10
	Bayern	8	3	33	4
	Hessen	-	-	-	-
	Niedersachsen	-	-	-	-
	Nordrh.-Westfalen	-	-	-	-
	Rheinl.-Pfalz	2	0	23	0
	Schleswig-Holstein	-	-	-	-
	Total	24	7	154	14
Bentazone	Baden-Wurttemb.	43	2	135	2
	Bayern	21	1	82	4
	Hessen	10	0	15	0
	Niedersachsen	15	0	50	0
	Nordrh.-Westfalen	36	3	65	3
	Rheinl.-Pfalz	5	1	15	2
	Schleswig-Holstein	11	0	36	0
	Total	141	7	198	11
Pyridate	Baden-Wurttemb.	8	0	31	0
	Bayern	5	0	25	0
	Hessen	5	0	32	0
	Niedersachsen	4	1	17	1
	Nordrh.-Westfalen	5	0	33	0
	Rheinl.-Pfalz	-	-	-	-
	Schleswig-Holstein	5	0	17	0
	Total	32	1	155	1
Chloridazon	Baden-Wurttemb.	18	0	40	0
	Bayern	21	1	82	1
	Hessen	10	0	21	0
	Niedersachsen	11	0	35	0
	Nordrh.-Westfalen	45	0	125	0
	Rheinl.-Pfalz	3	0	8	0
	Schleswig-Holstein	3	0	11	0
	Total	111	1	322	1

cont ...

TABLE 3 (continued)

Compound	State	Number of Wells sampled	Wells with Residues >0.1 µg/l	Water Samples Analysed	Water Samples with Residues >0.1 µg/l
CMPP	Baden-Wurttemb.	17	0	17	0
	Bayern	21	0	26	0
	Hessen	8	0	22	0
	Niedersachsen	1	0	1	0
	Nordrh.-Westfalen	43	0	50	0
	Rheinl.-Pfalz	5	1	26	2
	Schleswig-Holstein	-	-	-	-
	Total	95	1	142	2
1,2-Dich-loropropane	Baden-Wurttemb.	4	0	6	0
	Bayern	4	0	8	0
	Hessen	4	0	8	0
	Niedersachsen	1	0	2	0
	Nordrh.-Westfalen	4	0	5	0
	Rheinl.-Pfalz	-	-	-	-
	Schleswig-Holstein	13	4	95	24
	Total	30	4	124	24
Simazine	Baden-Wurttemb.	10	0	10	0
	Bayern	7	1	33	1
	Hessen	-	-	-	-
	Niedersachsen	-	-	-	-
	Nordrh.-Westfalen	-	-	-	-
	Rheinl.-Pfalz	3	0	23	0
	Schleswig-Holstein	-	-	-	-
	Total	20	1	66	1

Atrazine

All seven wells, in which atrazine was found in excess of the EEC MAC of 0.1 µg/l are shallow wells. The permeability of the soils is probably relatively high in all cases. The values above 0.1 µg/l occurred sporadically in the water samples taken at an average of 6 intervals.

Bentazone

Five of the eleven results above 0.1 µg/l are single isolated values. In one shallow well a series of four values above 0.1 µg/l was measured. However, little bentazone is used in this particular area and the actual values do not correlate with the use pattern of bentazone. The cause of the apparent contamination of the raw water therefore remains in doubt.

Pyridate

The single value found above 0.1 µg/l is one of a series which did not show any residues (ie. <0.05 µg/l) at four further sampling intervals. The well is a deep well. The well-specific information does not help with the interpretation of this result.

Chloridazon

The single value above 0.1 µg/l shown in Table 6 constitutes the only value for chloridazon above the limit of determination of 0.05 µg/l. This single, isolated value cannot be explained from the well-specific information. The value could not be confirmed by a second method and is therefore regarded as a false positive.

CMPP

Although the two positive results shown in Table 7 have not been confirmed by a second method, the totality of the analyses suggests that, on occasions, CMPP found in raw water can exceed the EEC MAC of 0.1 µg/l.

1,2-Dichloropropane

All 4 wells, in which 1,2-dichloropropane contamination above 0.1 µg/l was measured, are in the area of Pinneberg and Hamburg. In one case, agricultural use can be excluded as the cause for the contamination. In the other cases, the cause can either be the use as a soil disinfectant or the remaining burden of industrial plants which operated in the area in the past. No 1,2-dichloropropane contamination, even below 0.1 µg/l, was found in states other than Schleswig-Holstein.

Simazine

Simazine exceeded the EEC MAC of 0.1 µg/l ir a well in an area of low intensity agricultural usage. This factor taken in conjunction with the known environmental fate of simazine lead to the conclusion that its occurrence in the raw water cannot be explained by the normal movement of the a.i. in soil.

DISCUSSION

The results of the IPS monitoring programme have shown that it is difficult to achieve a high degree of analytical sensitivity with a high degree of reliability in trace-analytical methods.

It remains doubtful, if adequate analytical methods for all pesticides will be available by October 1989, the date at which the EEC MAC of 0.1 µg/l for pesticides in drinking water will need to be observed in the FRG. Particular doubts exist in cases where pesticides and their metabolites resemble natural substances. In any case, the methods will not be simple procedures in the sense of a quick and inexpensive routine analysis affording little personnel involvement.

As far as the processes of transport are concerned, which facilitate the leaching of chemicals into the groundwater, the programme has revealed a substantial need for further research, since it was often difficult

to establish a cause-effect-relationship in individual cases of contamination of drinking water with pesticides. Furthermore, it might be expected that parameters such as elevated nitrate levels would correlate with the extent and frequency of contamination of water with pesticides. However, such a correlation did not always occur (Iwan 1988).

The study has confirmed other reports that with the increasing sensitivity of analytical methods in recent years trace amounts of some pesticides in raw water (ground water) will be detected. Whilst the presence of pesticides in ground water may be associated with a variety of point sources, it has also become evident that ground water contamination can also occur as a consequence of regular and normal agricultural use. It is very likely that pesticides can occur in environmental compartments such as ground water at certain, though temporary concentrations. These concentrations most likely depend on the physico-chemical properties of the substances, the prevailing geological, pedological and meteorological conditions and the agricultural practices. For some pesticides, the concentration appears to be exceeding the present EEC MAC of 0.1 µg/l, for others they may be substantially below that level and analytically not (yet) detectable. Whilst the EEC MAC applies to drinking water, in practice drinking water produced from ground water undergoes in the majority of cases at present hardly any treatment which would reduce the amount of pesticides in the raw/ground water.

CONCLUSIONS

The need for the use of pesticides in modern agriculture for plant protection purposes is generally well recognised. Thus, the conflict of interest between the legitimate needs of agriculture and the quality standards imposed by the EEC Directive on the producers of drinking water was inevitable. This conflict is exacerbated by the awakening and, during the past few years, the extreme sensibilisation of the environmental consciousness, which has increased the interest in contaminants of ground and drinking water.

As already discussed, the MAC's of 0.1 µg/l and 0.5 µg/l for an individual pesticide and the total amount of any number of pesticides, respectively, are easily recognisable as arbitrary values. The lack of differentiation between individual representatives of this type of chemicals, which have widely differing biological and toxicological effects, is evidence for this. These values have no relation to the quantitative risk assessment on the basis of toxicological data.

In the absence of a toxicological base, reference is often made in the debate of the MAC's for pesticides to the principle of precautionary measures. However, the setting of zero or quasi-zero level moves away from the classical understanding of the precautionary principle, which aims at the elimination or prevention of dangers to humans and the environment deriving from immissions of substances. Instead, it aims at the protection of an environmental compartment from immissions of substances per se, which is obviously in conflict with the legitimate interest of agriculture.

The contamination of water, particularly drinking water, by chemicals including pesticides, is basically undesirable and should be avoided if at all possible. Realistically, however, because of the widespread use of pesticides and the ubiquitous occurrence of water sources a tiny proportion

of some pesticides can enter these water sources and can appear in drinking water. It is becoming impossible for almost any chemical from whatever source to escape detection in the environment if sufficient effort is made to do so. Therefore there is a need to be aware of the problem and to tackle it objectively using scientifically based principles.

The analytical limit of determination obviously cannot be regarded as a really relevent measure for the stipulation of the MAC's based on scientifically based principles. On the one hand, the analytical limit of determination of a substance is a "moving target", ie. continuous development leads to a lowering of the limit with time; on the other hand, the limit of determination is not indicative of any effects that might be exerted by the concentration of the substance determined at that limit.

The adequacy for human consumption of drinking water that contains traces of pesticides, is dependent on the actual levels found and their significance in the light of toxicological information available for the particular substance. The stipulation of an inflexible, single-value - and in particular at quasi-zero level - in the EEC Directive does not allow such a case-by-case assessment.

Indeed, the MAC for pesticides does, strictly speaking, not allow any assessment at all. Any residue above 0.1 µg/l is illegal and thus alleviating measures have to be taken regardless whether there is a hazard or not.

As long as agriculture and the water industry share the same "raw material" and environment for their respective industries, it is clear that a zero residue philosophy for pesticide residues in water is not a practical proposition. Therefore the MAC concept of the EEC Drinking Water Directive of a single quasi-zero value for all pesticides should be reconsidered and replaced by a concept of establishing individual values for each pesticide, which takes into consideration toxicological, ecological and agronomic aspects.

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METABOLISM OF AMITRAZ IN CITRUS

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ABSTRACT

Amitraz is a formamidine acaricide, widely used (as Mitac®) for control of mites on fruit and (as Tactic®) for control of ectoparasites on livestock. Metabolism work on this compound has proved technically difficult because of the chemical characteristics of the compound and its metabolites.

Metabolism of formulated [^{14}C]-amitraz was investigated in lemons grown under glass at Chesterford Park Research Station. At final harvest the applied radioactivity was quantitatively recovered, predominantly in the peel (86%). The total residue at harvest contained amitraz (18%), N-methyl-N'-(2,4-xylyl)formamidine (30%) and form-2',4'-xylidide (7%). 12% of the residue consisted of conjugates of 4-amino-m-toluic acid and a further 8% was metabolites convertible to 2,4-dimethylaniline.

INTRODUCTION

Previous studies into the metabolism of amitraz on citrus established that the residue at final harvest contained a large proportion of unidentified polar and bound material. In addition, the parent compound was found to be unstable towards even traces of acid, while some of its metabolites were unstable under moderately basic conditions.

This paper describes the extraction method developed to maintain the integrity of these sensitive compounds and also to reduce the bound portion. Analytical procedures designed to characterise the polar residue are also described.

MATERIALS AND METHODS

Treatment and harvest of fruit

Lemons (variety Eureka on Poncirus rootstocks) were given two treatments, 4 weeks apart, using [U-^{14}C-phenyl]-amitraz (specific activity 20 μCi/mg) formulated as an emulsifiable concentrate and diluted with water to the normal field rate concentration of 1.64 mg/ml. The trees were maintained under glasshouse conditions with a photoperiod of 16 hrs. After a pre-harvest interval of 2 weeks, the mature lemons were harvested in samples of 3.

Extraction of fruit

Samples of fruit were dipped in 5% triethylamine (Et_3N)/hexane before being divided into peel and flesh, which were then analysed separately.

The plant material was extracted by maceration with solvent (twice

volume:tissue weight) for 2 minutes using a Waring Blender, followed by filtration.

The peel was extracted with 5% Et_3N/hexane and both the peel and the flesh were extracted with 5% Et_3N/acetone and 50% methanol/water. The radioactivity in the extracts was quantified by liquid scintillation counting. The radioactivity in the solid residue was determined by combustion and liquid scintillation counting of the resulting $^{14}CO_2$.

Chromatography of extracts

The extracts were concentrated by Buchi Rotavapor to low volume and the recovery was checked by liquid scintillation counting. The concentrated extracts were, if possible, applied directly to the pre-absorption zone of Macherey-Nagel GUV (0.25 nm) silica plates, having been underspotted with a mixture of standard compounds (Figure 1). The solvent systems were chosen from the following:

1 hexane/Et_3N (17:3)
2 cyclohexane/ethylacetate/Et_3N (5:3:2)
3 ethylacetate/isopropanol/water (65:23:12)
4 chloroform/methanol/acetic acid (10:0.75:0.1)

Radioactive bands were quantified using an Isomess RITA Linear Analyser; co-chromatography with standard compounds was confirmed by autoradiography. The radioactive regions on preparative scale plates were de-lineated using a Berthold LB 292 Beta camera. The major radioactive regions could then be scraped off and extracted by repeated ultrasonication with methanol followed by filtration.

Flash chromatography was conducted by 'slurry-packing' silica (Kieselgel 60H) in Et_3N/hexane (1:99), in a glass column with sinter. The extract was applied to the top of column in a small amount of hexane and eluted at a pressure slightly above atmoshperic using Et_3N/hexane (1:99). Fractions of eluant were collected and sampled for LSC. A histogram was prepared from the results and the fractions containing the majority of the radioactivity were re-chromatographed on TLC in System 1.

Hydrolysis of extracts by acid

An aliquot of the concentrated extract in a Reacti-vial was diluted with 6M HCl to give a solution with a final concentration of 4.5M in hydrochloric acid. The vial was sealed and heated at approximately 91°C for 4.5 hours. The mixture was cooled and adjusted to pH 2 with 2M sodium hydroxide. The mixture was extracted 4 times with approximately equal volumes of water saturated N-butanol, which was then concentrated before TLC analysis.

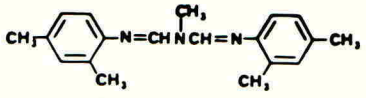
Hydrolysis of extracts by acid and alkali

The concentrated extracts were diluted with an equal volume of 2M HCl (giving a final concentration of 1M in HCl) before being heated at reflux for 3 hrs in a round-bottom flask fitted with a double walled condenser. In between the flask and the condenser was a liquid-liquid extractor containing 20 ml distilled water and 50 ml hexane, designed to trap any volatiles which may have been produced. When the solution in the flask had

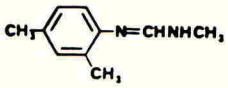
been cooled, an amount of solid sodium hydroxide was added, calculated to give a final concentration of 1M in NaOH. 10 drops of antifoam were added and the mixture was then heated at reflux for a further 8 hrs. The alkaline solution was extracted at pH 10 with water saturated n-butanol (4 times) and at pH 2 with ethylacetate (4 times) and water saturated n-butanol (4 times). Recoveries were checked by LSC and the organic extracts were then concentrated by Rotavapor before TLC analysis.

FIGURE 1

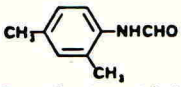
Structures of standard compounds



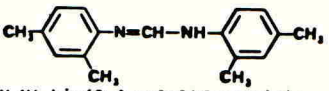
I N-methylbis(2,4-xylyliminomethyl)amine



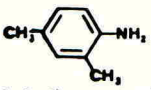
II N-methyl-N'-(2,4-xylyl)formamidine



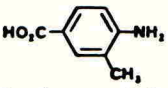
III Form-2',4'-xylidide



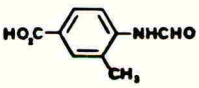
IV N,N'-bis(2,4-xylyl)formamidine



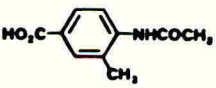
V 2,4-dimethylaniline



VI 4-amino-m-toluic acid



VII 4-formamido-m-toluic acid



VIII 4-acetamido-m-toluic acid

Radio-gcms of extracts

Samples were analysed on an AI 93 Gas Chromatograph fitted with 25 mtr QC5/BPI, 0.53 mm ID (OVI equivalent) column, using a temperature gradient of 75-200°C at 20°C/minute.

The radioactivity was detected by an ESI Panax Anti-Coincidence Ratemeter and the mass spectra were determined by a Finnegan Ion Trap Detector.

RESULTS AND DISCUSSIONS

At final harvest, all the applied radioactivity was recovered, of this less than 4% remained bound. (All results are summarised in Table 1).

Over 18% of the radioactivity was recovered from the fruit surface (Extract A) and was found by TLC in Systems 1 and 2 to be principally unchanged amitraz (I). The majority of the remaining radioactivity in the fruit was associated with the peel, less than 15% penetrating into the flesh.

TABLE 1

Summary of metabolite analysis expressed as a percentage of total recovered radioactivity

Metabolites	Peel extracts				Flesh extracts		Total
	A (18.2%)[5]	B (36.4%)[5]	C (22.0%)[5]	D[3] (5.4%)[5]	E (13.7%)[5]	F (0.6%)[5]	
Amitraz	15.7	2.4	-	-	-	-	18.1
II (Free)	0.9	18.0	2.2	-	8.2	-	29.3
(Conjugated)	-	-	-	0.2	-	-	0.2
III (Free)	0.5	3.2	0.3	-	0.7	-	4.7
(Conjugated)	-	-	2.1[2]	0.5			2.6
IV (Free)	0.2	0.9	-	-	0.6	-	1.7
(Conjugated)	-	-	1.6[2]	0.2	-	-	1.8
V (Free)	-	-	-	-	-	-	-
(Conjugated)	-	8.0[1]	-	0.3	-	-	8.3
VI (Free)	-	-	-	-	-	-	-
(Conjugated)	-	-	4.5[2]	0.2	-	-	4.7
VII (Free)	-	-	1.1	-	0.3	-	1.4
(Conjugated)	-	-	1.1[2]	0.5	-	-	1.6
VIII (Free)	-	-	1.1	-	1.5	-	2.6
(Conjugated)	-	-	1.4[2]	0.1	-	-	1.5
Polar[4]	0.5	0.6	-	0.5	1.7	-	3.3
Remainder[4]	0.4	3.3	6.7	2.8	0.8	0.6[6]	14.6
Bound	-	-	-	-	-	-	3.8

Key to extracts

A Surface wash
B Et_3N/hexane extract of peel
C Et_3N/acetone extract of peel
D Methanol/water extract of peel
E Et_3N/acetone extract of flesh
F Methanol/water extract of flesh

1 From the hydrolysis of the non-polar unknown (Metabolite 1) by acid and base.
2 Percentages calculated from acid hydrolysis of polar material after preparative TLC.
3 Percentages calculated from acid/base hydrolysis of whole extract
4 No single component represented >1% of total sample.
5 Figures in brackets are percentage that the extract represents of total activity in sample.
6 Extract not analysed.

Analysis of the Et_3N/hexane extract of the peel (Extract B, 33.1%) showed N-methyl-N'-(2,4-xylyl)formamidine (II) to be the major metabolite, with traces of amitraz (I), form-2',4'-xylidide (III) and N,N'-bis(2,4-xylyl)formamidine (IV). An unknown (Metabolite I) was also apparent running just above amitraz in System 1. Metabolite I was purified by flash chromatography (see Materials and Methods), but despite the application of a wide range of physical and chemical techniques, it remained unidentified. It was therefore subjected to the standard residue method of acid/base hydrolysis (see Materials and Methods), designed to convert amitraz (I) and all its previously identified metabolites (II, III, IV) to 2,4-dimethylaniline. Analysis of the volatiles trap from the hydrolysis (containing over 95% of the recovered radioactivity) by radio-gcms confirmed the product as 2,4-dimethylaniline (V).

The Et_3N/acetone extract of the peel (Extract C, 22.0%) was found to be a complex mixture of metabolites and natural product co-extractives. The initial clean-up was by preparative TLC. The identity of the radioactive bands corresponding to II and III was confirmed by elution from the silica and re-chromatography against standards. The majority of the activity on the plate however, was at or close to the origin and so after elution from the silica the mixture of polar compounds was acid hydrolysed (see Materials and Methods). n-Butanol extracted over 93% of the radioactivity from the hydrolysate and chromatography in Systems 3 and 4 confirmed the principal product as 4-amino-m-toluic acid (VI) with small amounts of II, III, IV, 4-formamido-m-toluic acid (VII) and 4-acetomido-m-toluic acid (VIII). The remainder was composed of at least 8 components each less than 1% of total residue.

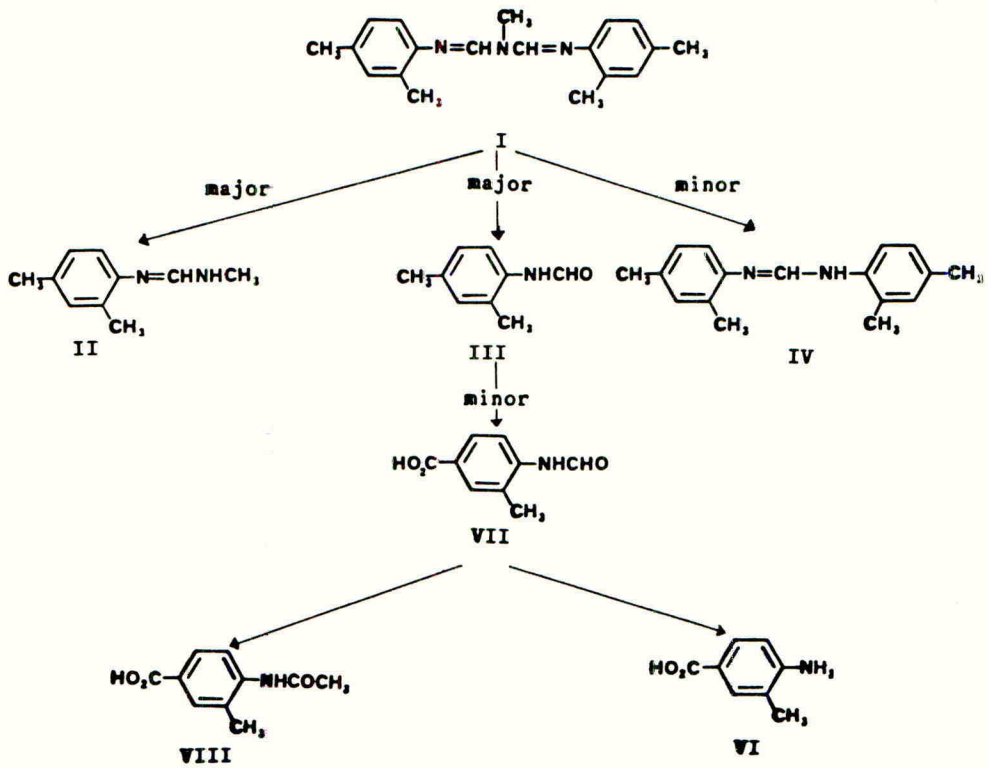
The methanol/water extract of the peel (Extract D, 5.4%) was found to contain principally polar material and so was acid/base hydrolysed directly. 10% of the radioactivity was recovered in the volatiles trap and was identified by radio-gcms as V. The aqueous hydrolysate was partitioned at pH 10 and 2 and although there was interference from charred plant material, TLC of the resulting organic extracts in Systems 3 and 4 found traces of all the metabolites (see Table 1).

The concentrated Et_3N/acetone/flesh extract (Extract E, 13.7%) required partitioning into n-butanol at pH 2 prior to analysis. TLC in Systems 3 and 4 demonstrated it to be almost entirely compound II.

The methanol/water/flesh extract (Extract F, 0.6%) contained insufficient activity for analysis. The proposed metabolic profile for amitraz in lemons is shown in Figure 2.

FIGURE 2

Metabolic profile of amitraz in lemons



CONCLUSION

All of the applied radioactivity was recovered at final harvest, of which over 96% was extractable.

The final residue consisted of unchanged amitraz (18.1%), N-methyl-N'-(2,4-xylyl)formamidine (II) (29.5%), form-2'4'-xylidide (III) (7.3%) and N,N'-bis(2,4-xylyl)formamidine (IV) (3.5%). Metabolic oxidation of the 4-methyl group to the acid gave rise to 4-amino-m-toluic acid (VI) (4.7%), 4-formamido-m-toluic (VII) (3.0%) and 4-acetamido-m-toluic acid (VII) (4.1%), present mainly as conjugates. Hydrolysis of unknowns converted a further 8.3% to 2,4-dimethylaniline (V), leaving several minor components each less then 1% of total recovered radioactivity.

ACKNOWLEDGEMENTS

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THE METABOLISM OF CYCLOXYDIM IN SOYBEANS

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ABSTRACT

Cycloxydim is a new selective graminicide for use in broad-leaf crops. The transformation of this compound in soybean has been investigated and found to be very complex. Cycloxydim is rapidly metabolized in plants and four series of different types of metabolites in either free or conjugated forms are formed, depending on which plant part - forage/straw or seed - is investigated. The transformation products are formed by chemical and/or enzymatic reactions involving a range of oxidations, a rearrangement, and cleavage of the cyclohexenone ring or the ethoximino side-chain. The latter reaction may also have been initiated by light.

INTRODUCTION

Cycloxydim, 2-[1-ethoxyimino)butyl]-3-hydroxy-5-(3-thianyl)-2-cyclohexen-1-one (Figure 1), the active ingredient of the trade products "Focus", "Laser" and "Stratos", has been developed by BASF for the post emergence selective control of both annual and perennial grasses in broadleaf plants. This compound readily enters the plant and translocates extensively. During its development, the metabolic fate of cycloxydim in soybeans was investigated using the [cyclohexenone-4,6-^{14}C]-labelled material. This paper deals with the structural transformations of cycloxydim in this crop.

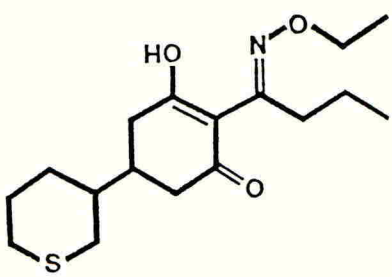


Figure 1. 2-[1-Ethoxyimino)butyl]-3-hydroxy-5-(3-thianyl)-2-cyclohexen-1-one, abbreviated designation: TS

MATERIALS AND METHODS

Reference compounds

Non-radiolabelled reference compounds were synthesized to facilitate the identification of the metabolites formed. The respective structures and their abbreviations are tabulated in Figure 2.

Crop and spraying

Soybean plants (3-5, variety SRF 450) were grown in twenty five pots containing a 3:1 Limburgerhof sandy soil/peat mixture. At the 2 leaf stage the plants were hand-sprayed with an aqueous suspension of an EC formulation of ^{14}C-cycloxydim; the specific radioactivity was 399 MBq/mmole. The amount of cycloxydim applied corresponded to 0.2 kg/ha, which is the recommended application rate. An adjuvant, equivalent to 1.5 l/ha of an oil concentrate (Ad Plus 411) was admixed with the spray solution.

The soybean plants were grown under controlled conditions in a phytotron (Heraeus-Vötsch) with xenon arc light (lighting 24000 lux for 14 hours per day, relative humidity 70%/90%, temperature 25° C/17 °C during day/night, respectively) and harvested shortly after spraying, and at 7, 14, 21, 40 and 82 days post treatment. Up to 40 days the samples corresponded to the forage stage, whereas at 82 days post treatment straw and seed samples were collected. Prior to analysis, the samples were stored at -21 °C.

Isolation of metabolites

Metabolites in the foliage and in the seed were efficiently extracted by aqueous methanol (7/3 and 1/1 v/v, respectively). After removal of the methanol under reduced pressure, the remaining aqueous phases were partioned between dichloromethane and water, after adjusting firstly to alkaline and then acidic pH values. It was expected that at least the parent and its sulphoxide and sulphone derivatives (TSO, TSO_2) would exhibit acidic properties so that neutral and alkaline transformation products could be separated into different fractions by this approach.

About half of the radioactive residues in the aqueous phases from the foliage were not partitioned into dichloromethane at all, indicating conjugated and/or very polar materials. After hydrolysis with 10% aqueous HCl for 2 hours at 40 °C, ethyl acetate extracted appreciable amounts of radioactivity. Also, after lyophilization of the aqueous phase, reaction for 15 hours at room temperature with 10% sulphuric acid acid in methanol and subsequent dilution with water then allowed most of the radioactivity to be directly extracted into dichloromethane.

Unextracted radioactivity remaining in the foliage and seeds was fractionated according to Huber and Otto (1983).

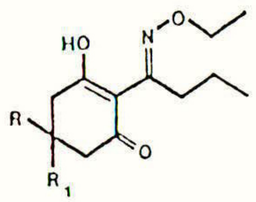
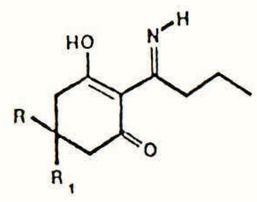
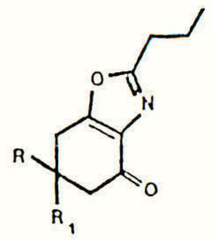
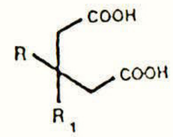
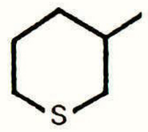
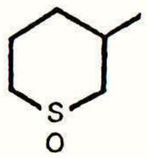
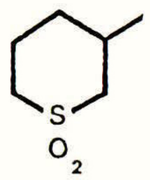
R	R_1				
	H	TS	T1S	T2S	TGS
	H	TSO	T1SO	T2SO	TGSO
	OH	5-OH-TSO		6-OH-T2SO	OH-TGSO
	H	TSO_2	$T1SO_2$	$T2SO_2$	$TGSO_2$
	OH	5-OH-TSO_2		6-OH-$T2SO_2$	OH-$TGSO_2$

Figure 2. Synopsis of cycloxydim metabolites/reference standards and abbreviations used

Chemical reactions to aid in identifications

Beckmann rearrangement reaction

For chemical structure confirmation, the metabolites TSOx (x = 1 or 2) and their 5-OH-analogues contained in the acidic dichloromethane extracts, were heated with 5% aqueous methanolic ascorbic acid under reflux. By this treatment they were quantitatively rearranged (Beckmann rearrangement) to T2SOx and the corresponding 6-OH-analogues. The sulphoxide metabolites were then further oxidized by m-chloroperbenzoic acid to $T2SO_2$ and 6-OH-$T2SO_2$, respectively, which were volatile and therefore could be analysed by gas chromatography-mass spectrometry.

Oxidative cleavage

All metabolites still containing the intact cyclohexenone ring could be cleaved/oxidized by alkaline hydrogen peroxide to $TGSO_2$. The latter was easily methylated and was then amenable to gas chromatgraphic analysis. It is to be noted, that excess hydrogen peroxide was carefully destroyed prior to further work up of the oxidation batches.

Analytical methods

Organo-soluble and aqueous extracts were radioassayed by liquid scintillation counting (lsc). Radioactive residues left after extraction were quantified by combustion (Packard, Model 306, Sample Oxidizer) and lsc. The organo-soluble extracts were concentrated *in vacuo*, and then analysed by radio thin layer chromatography and/or radio high pressure liquid chromatography (normal phase silica). Metabolites were also isolated and purified by high pressure liquid chromatography and their structures confirmed by mass spectrometry or gas chromatography-mass spectrometry (Finnigan 3200).

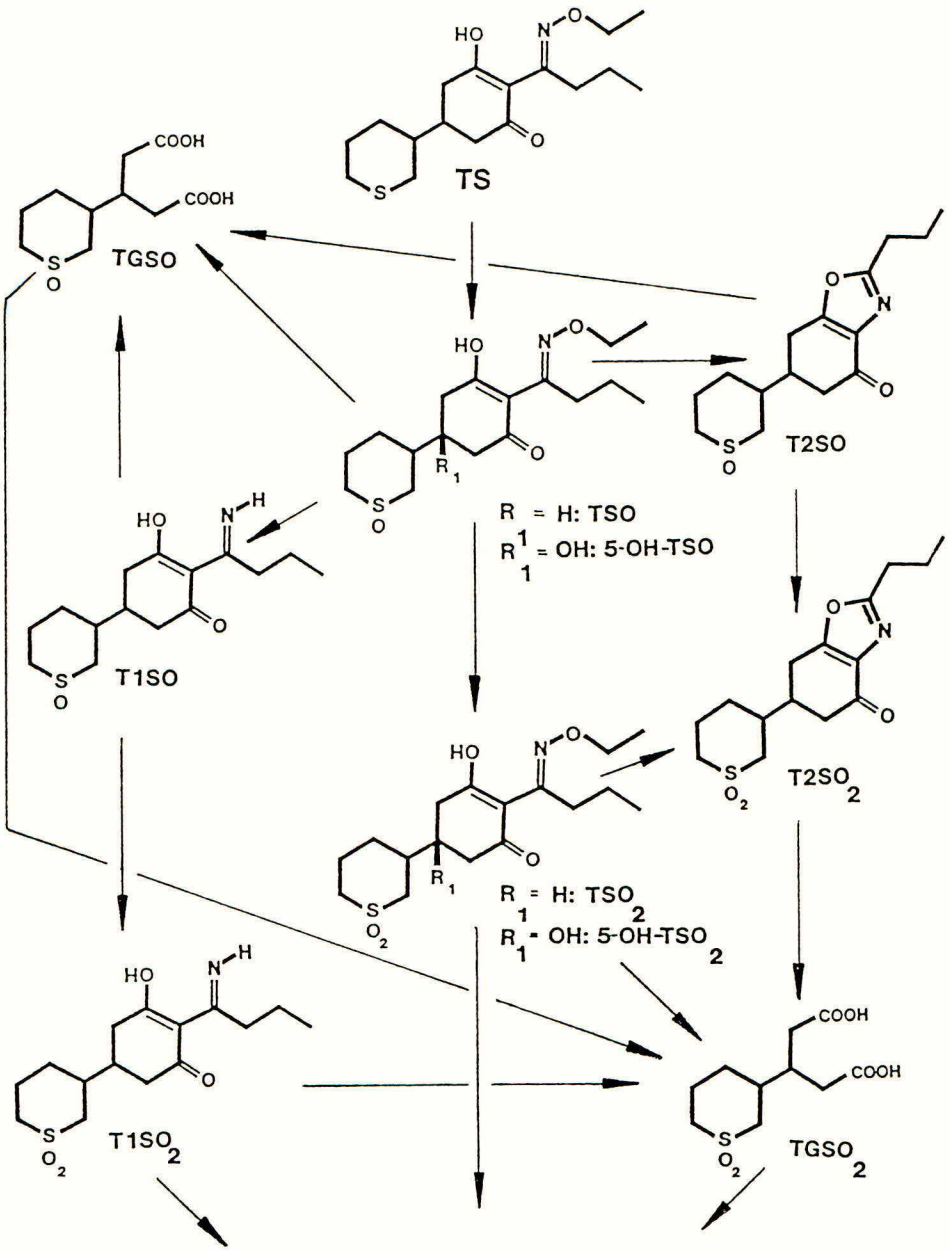
RESULTS AND DISCUSSION

Results

In the foliage the active ingredient was very labile and oxidized within hours to its sulphoxide TSO. Further important metabolites were conjugated TGSO and $TGSO_2$. Minor metabolites were TSO_2, $T1SO_2$, T2SO, and $T2SO_2$. These transformation products were extensively metabolized and partly incorporated into lignin fractions.

In mature soybean seeds TSO was the major metabolite, followed by T2SO, 5-OH-TSO and 5-OH-TSO_2. The two latter hydroxylation products appeared in about equal amounts. Minor metabolites were $T1SO_2$ and $T2SO_2$. The hydroxy analogues of T2SOx, namely 6-OH-T2SOx were not found as metabolites. Radioactivity was also incorporated in protein precipitates indicating again extensive further transformation of cycloxydim and its metabolites.

On the basis of the results discussed above a metabolic pathway for cycloxydim in soybean can be drawn, see Figure 3.



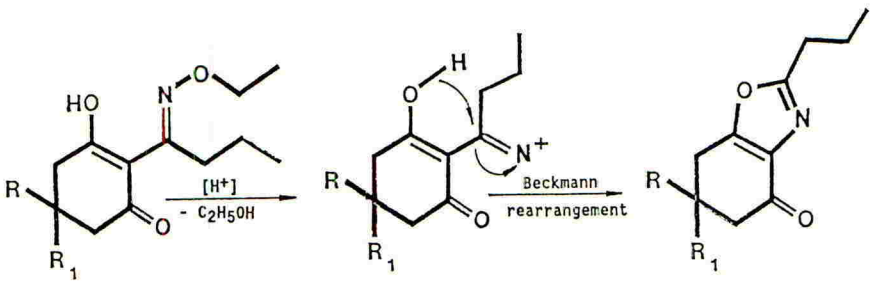
NB: TSO and T2SO occur free and conjugated, TGSO and $TGSO_2$ only conjugated, all others free

Figure 3. Metabolic pathway of cycloxydim in soybeans

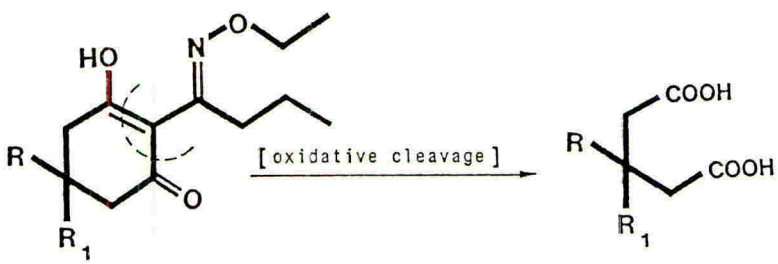
Discussion

The sulphur atom in cycloxydim was readily oxidized on/in the soybean. Therefore only trace amounts of the cycloxydim were detected shortly after spraying (0 day sample). Other unoxidized metabolites such as T1S and T2S did not appear. The predominant oxidation products were the sulphoxide and sulphone metabolites (TSOx) and their hydroxylated analogues (5-OH-TSOx).

The next important transformation was the Beckmann rearrangement reaction. Only TSOx metabolites were rearranged, not the 5-OH-derivatives. The rearrangement was either proton or heat catalyzed. A possible mechanism is presented as follows.

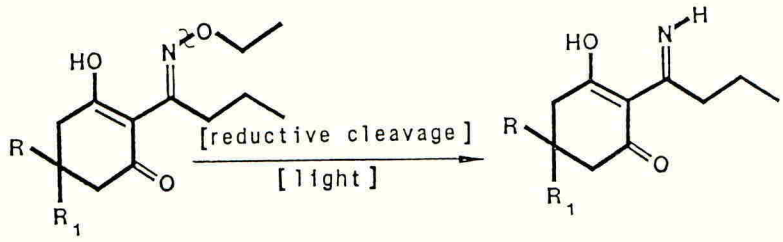


Another interesting metabolism reaction is the oxidative cleavage of the cyclohexenone ring to form the glutaric acid derivatives TGSO and $TGSO_2$ in the foliage.



This reaction can also be carried out chemically with hydrogen peroxide under alkaline conditions. Such a reaction of cyclic 1,3 diones (the tautomeric form of the hydroxy cyclohexenone ring) with hydrogen peroxide is well known (Hesse 1978). Using this reaction the metabolites containing the cyclohexenone ring - including the Beckmann rearangement products T2SOx - can all be converted to two similar compounds i.e. $TGSO_2$ and OH-$TGSO_2$. The heterocyclic ring is stable to the reaction conditions used. The two di-carboxylic acids formed are both easily methylated with either diazomethane or methanol/sulphuric acid. Such methylation yields compounds which are amenable to analysis by gas chromatography. This sequence of reactions has been found useful in the development of a residue analytical method using a "common moiety" approach to determine the total residue present.

Cleavage of the ethoximino group has also been found to occur in plants.



It is possible that enzymes are responsible for this transformation. However, this reaction could also be initiated photochemically, since the two imines, TISO and $TISO_2$, are formed in high yield when aqueous solutions of cycloxydim are irradiated with a xenon arc source (simulating sunlight).

Metabolites were detected both free and as conjugates (see Figure 3). Enzymes cleaving glucoside conjugates were successful in cleaving the conjugated metabolites, indicating the probable nature of the conjugating endocon. However, for conjugates of TGSOx cleavage and methylation with 10% sulphuric acid in methanol was much more effective and reproducible. This latter reaction also generated volatile esters which could be readily analysed by gas chromatography and gas chromatography-mass spectrometry.

Finally, in soybeans the hydroxylated metabolites were only formed in the seeds and were not found in the foliage either at the forage stage or in straw samples.

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THE DEGRADATION AND LEACHING OF SN 539 865 IN SOIL - ELUCIDATION OF THE DEGRADATION PATHWAY BY USE OF THREE SEPARATE RADIOLABELLED POSITIONS

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ABSTRACT

SN 539 865 is a quinazoline fungicide containing three major ring moieties. Studies in soil have therefore been conducted with [^{14}C] radiolabelling in each of the rings, in order to fully elucidate the degradation pathway. Degradation of SN 539 865 proceeded steadily under both aerobic and anoxic soil conditions with a 'half-life' of between 2½ and 5 months. Under aerobic conditions each ring moiety was mineralised to $^{14}CO_2$ at a different rate. Virtually no $^{14}CO_2$ was produced under sterile soil conditions. Two major degradation products 3-(2,4-dichlorophenyl)-2, 4(1H,3H)-quinazolinedione and 1,2,4-triazole have been characterised by tlc and hplc and identified by radio gc-ms. Work continues on other degradation products.

Leaching studies have been conducted in the laboratory, using soil thick layer plates and soil columns (with collection of volatile products) and outdoors using intact lysimeter cores 10.5 cm internal diameter x 1 m deep. SN 539 865 had low mobility under all experimental conditions.

INTRODUCTION

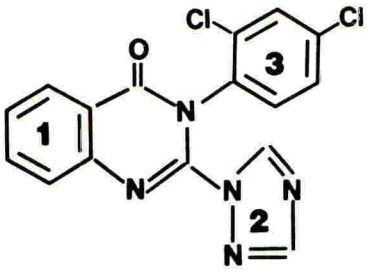
SN 539 865 is a quinazoline fungicide containing a triazole and two other ring moieties. In order to fully elucidate the degradation pathway three radiolabelled forms were prepared with [^{14}C] uniform labelling in each of these major ring structures, see Figure 1.

An environmental safety assessment has been conducted which included an examination of the degradation and mobility of SN 539 865 under a variety of soil conditions.

Degradation has been investigated in the laboratory under aerobic, anoxic and sterile soil conditions. In addition, mobility has been studied in the laboratory using soil thick layer plates, soil columns (with the collection of volatiles) and outdoors using intact lysimeter cores.

FIGURE 1

SN 539 865



3-(2,4-dichlorophenyl)-2-(1H-1,2,4 triazol-1-yl)-4(3H)-quinazolinone.

1 = U-[^{14}C] Benzyl label
2 = U-[^{14}C] Triazole label
3 = U-[^{14}C] Dichlorophenyl label

MATERIALS AND METHODS

Degradation studies

SN 539 865 was applied at up to 1.0 kg ai/ha to four contrasting soil types, two sandy loams, a silty clay loam and a clay, all collected fresh from the field and each with no history of previous pesticide treatment. The soils were incubated at 20°C in the dark at 40% of their moisture holding capacity and continuously flushed with carbon dioxide-free moist air. The air was sterilised by in-line filters for the sterile soils, which were sterilised prior to treatment by autoclaving at 15 psi (121°C) for two 20 min periods, 24 hours apart. Anoxic conditions in non-sterile treatments were established by flooding with a water layer, at least 2.5 cm deep, at the time of treatment. Volatile products, including $^{14}CO_2$, were collected in a series of 'trapping' solutions comprising of ethanediol, 0.1M sulphuric acid and ethanolamine respectively. Immediately after treatment and at various intervals up to 12 months, either duplicate or triplicate flasks of soil were taken for extraction and analysis.

Mobility studies

a) Soil thick layer chromatography plates

The mobility of [^{14}C]-benzyl SN 539 865 and two of its soil metabolites [^{14}C]-3-(2,4-dichlorophenyl)-2,4(1H,3H)-quinazolinedione (FBC 96 215) and [^{14}C]-1,2,4 triazole have been investigated in four contrasting soil types (sand 0.6% organic matter, silty clay loam 5.5% organic matter, clay 8.4% organic matter and sandy loam 3.2% organic matter). [^{14}C]-Atrazine, a compound known to be of intermediate mobility, was used as a reference in these leaching studies. The soils were spread uniformly on stainless steel plates 0.5 cm deep, 5 cm wide and 30 cm long. The radiolabelled compounds were mixed with soil, applied at 2 cm from one end and leached with 80 ml of 0.01M $CaCl_2$ solution, the leachates being collected and radioassayed. The leaching profiles were assessed using radioscanning followed by removal of soil segments, solvent extraction and combustion of the remaining soil.

b) 'Aged' leaching in soil columns

The mobility of [^{14}C]-benzyl SN 539 865 and [^{14}C]-triazole SN 539 865 has been investigated after 30 days aerobic incubation in two soil types, a sandy loam (2.6% organic matter) and a clay (14.4% organic matter). After the ageing period the treated soils containing parent compound and metabolites were transferred to the top of glass columns (30 cm high) of the corresponding soil type and leached with approximately 1100 ml (0.01M $CaCl_2$) over a 30 day period. During both the ageing and leaching periods volatile products evolved from the soil surface were collected in a series of trapping solutions. Leachate was collected and radioassayed on a daily basis. At the end of the leaching period the columns were divided into 5 cm segments and each segment analysed.

c) Intact lysimeter cores

In order to investigate the competing mechanisms of degradation and mobility under outdoor conditions lysimeter experiments were conducted as described previously (Leake et al. 1987). Intact lysimeter cores (10.5 cm i.d. x 1 m deep) were collected in plastic pipes using a 'Copco' hammer drill to sink the pipes into the ground. Two soil types, a sand (with low organic matter) and a sandy loam soil were collected. Each lysimeter core was fitted with a Buchner funnel containing acid washed sand and supported outdoors in a glass fibre tank. Triplicate columns of each soil type were treated with [^{14}C]-benzyl SN 539 865 and leachate collected over the period of 1 year. The columns were then cut into 10 cm segments and analysed.

Radiochemical analysis

Soil samples and segments were extracted under soxhlet conditions with 300 ml dichloromethane followed by 300 ml acetonitrile/water (80/20). The radioactivity in liquid extracts and volatile traps was quantified by liquid scintillation counting (LSC).

The soil samples were then dried at room temperature, ground to a fine powder and portions taken for combustion prior to quantification by LSC. These procedures enabled a radiochemical recovery to be obtained for each treated soil sample in all studies except the lysimeters where no volatile products were collected.

Chromatographic analysis

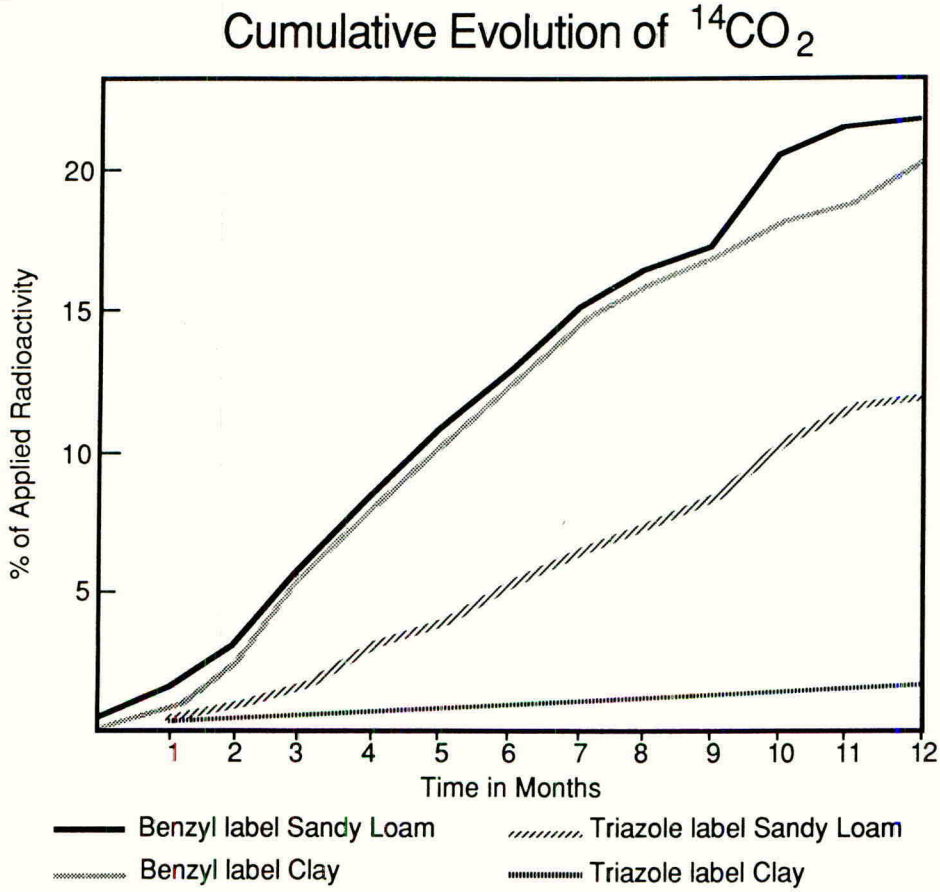
Following concentration by rotary evaporation, when required, the soil extracts were analysed by thin layer chromatography, (tlc, using both 'normal' and 'reverse' phase C_{18} bonded plates) and high performance liquid chromatography (hplc). Authentic samples of postulated metabolites were used as chromatographic references. The relative positions of the reference compounds on tlc were located by visualisation under uv light, and the radiolabelled products by linear analyser scanning and autoradiography with non-screen X-ray film. Identification of SN 539 865 and the two major metabolites FBC 96 215 and 1,2,4-triazole was obtained by radio gc-ms.

RESULTS

Degradation of SN 539 865 in soils

The degradation of SN 539 865 proceeded steadily under aerobic conditions with a 'half-life' of 2½ months in the sandy loam and 5½ months in the silty clay and clay soils. Initially, the majority of the applied radioactivity was extractable with dichloromethane. However, the radiocarbon remaining 'bound' to the soils gradually increased with time with up to 40% (after 12 months) in the [^{14}C]-benzyl SN 539 865 treatment and 47% (after 9 months) in the [^{14}C]-triazole treatments respectively. A proportion of the applied radiochemical was completely mineralised to $^{14}CO_2$ (up to 20% after 1 year) (see Figure 2). There was no $^{14}CO_2$ produced from sterile soils. In general, there was good agreement in the rate of decline between the three radiolabelled treatments of SN 539 865.

Figure 2.



The soil extracts contained two major radioactive degradation products. These compounds were identified as 3-(2,4-dichlorophenyl)-2,4(1H,3H)-quinazolinedione (FBC 96 215) and 1,2,4-triazole. [^{14}C]-FBC 96 215 was observed in both [^{14}C]-benzyl and [^{14}C]-dichlorophenyl labelled SN 539 865 treatments accounting for up to 14% in aerobic soils. However under flooded conditions, where there was a significantly reduced rate of mineralisation of [^{14}C]-FBC 96 215 to $^{14}CO_2$, quantities steadily increased to around 42% after 6 months. Under sterile conditions, SN 539 865 was slowly degraded to [^{14}C]-FBC 96 215 indicating that cleavage of the triazole moiety was partially hydrolytic. Several other compounds remain to be identified from [^{14}C]-triazole SN 539 865 treatments, where released 1,2,4-triazole undergoes further biodegradation.

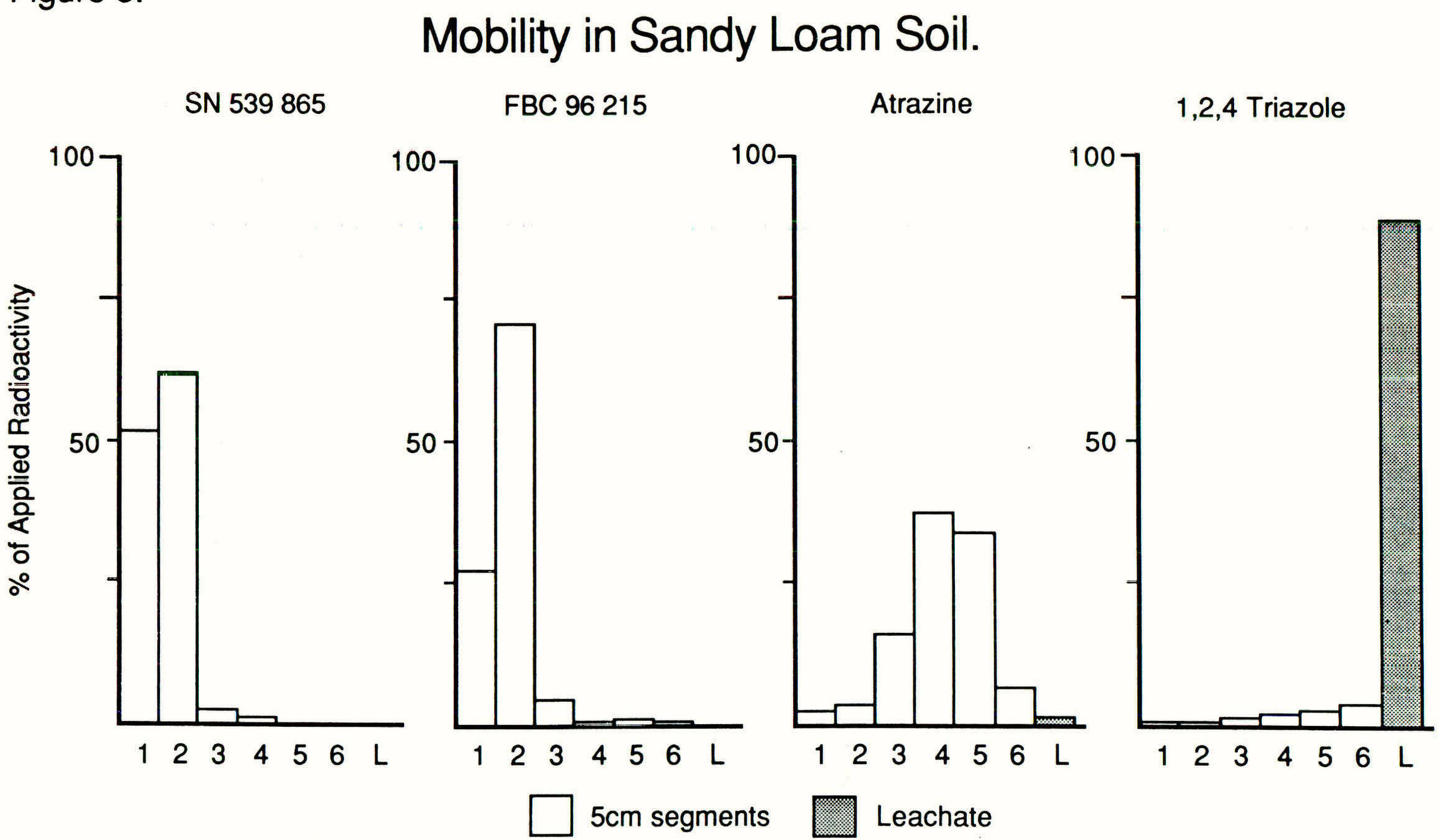
Mobility of SN 539 865 in soil

The degree of adsorption and therefore the extent of mobility of a non-ionic pesticide in soil can be calculated from its octanol/water partition coefficient (Log P) (Briggs 1981). Measured Log P values for SN 539 865 and FBC 96 215 were 3.2 by shake flask method and 3.0 (by hplc) respectively. These agreed well with estimations of Log P values using the Log P3 (MedChem, Pomona College) program which for SN 539 865, FBC 96 215 and 1,2,4-triazole were 3.0, 3.0 and zero respectively. These results predicted that both SN 539 865 and FBC 96 215 would be generally of low mobility whereas 1,2,4-triazole would be more mobile.

Using soil thick layer plates SN 539 865 and FBC 96 215 had very similar mobilities in four contrasting soil types ranging from immobile in silty clay loam and clay soils to mobile in the sand with low organic matter content. In contrast 1,2,4-triazole was more mobile in all four soil types see Figure 3. Atrazine, as expected showed intermediate mobility. The results were therefore in good agreement with predicted mobilities see Table 1.

In the [^{14}C]-benzyl SN 539 865 aged soil treated columns the majority of the radioactivity remained in the 'aged' treated soil on the top of the column. Some movement into the top 5 cm segment of untreated soil was observed, particularly in the sandy loam soil. Less than 0.2% and 0.6% of applied radiochemical was collected in total in the leachate from the clay and sandy loam soils respectively. Up to a total of 6% of applied radioactivity was collected as $^{14}CO_2$ during both the ageing and leaching periods, and a good total recovery of radioactivity was obtained. This result confirmed the relatively low mobility of SN 539 865.

Figure 3.


Mobility in Sandy Loam Soil.
SN 539 865
FBC 96 215
Atrazine
1,2,4 Triazole
% of Applied Radioactivity
100
50
1 2 3 4 5 6 L
5cm segments
Leachate

Similarly with the [^{14}C]-triazole SN 539 865 aged soil treatments the majority of the applied radioactivity remained in the treated soil layer. Some movement into the top 5 cm segment occurred, particularly in the sandy loam soil. However, up to 6% and 19% of applied radioactivity was collected in total in the leachate from the clay and sandy loam soils respectively. This was shown to be [^{14}C]-1,2,4-triazole.

Results from the lysimeter studies confirmed those from the laboratory, showing low mobility of the parent compound and ^{14}C-benzyl labelled degradation products in both a sandy loam and sand (with low organic matter) soils. Over the 12 month study period less than 0.5% of applied radioactivity was collected in the leachate, the majority of the radiochemical remaining in the top 10 cm segment. A study with [^{14}C]-triazole SN 539 865 is currently in progress.

TABLE 1

Comparison of predicted mobility with experimental data

	Sand	Silty clay loam	Clay	Sandy loam
% organic matter content	0.6	5.5	8.4	3.2
SN 539 865		Helling Index	Helling (1971)	
Predicted	3	1	1	2
Measured	3	1	1	2
FBC 96 215				
Predicted	3	2	1	2
Measured	4	1	1	2
1,2,4-triazole				
Predicted	5	4	4	4
Measured	5	5	5	5

Helling Index 1 = Immobile 2 = Low 3 = Intermediate
4 = Mobile 5 = Very mobile

CONCLUSION

The use of three separate radiolabelled positions within the molecule has enabled a greater understanding of the fate of each component of the molecule in soil. SN 539 865 was degraded by both chemical hydrolysis and the activity of soil microorganisms, hence it is unlikely to persist in the environment.

SN 539 865 and the major soil metabolite FBC 96 215 have been shown to have low mobility in both laboratory and outdoor studies and are therefore unlikely to contaminate ground water. However the 1,2,4-triazole degradation product has been shown to more mobile in laboratory studies and further studies are underway under outdoor conditions to more accurately assess the combined processes of degradation and leaching.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the contributions of colleagues who have helped on these projects, in particular Mr I Morton.

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