

Australian Cotton Cooperative Research Centre  
Environmental Protection: Pesticides

# COTTON PESTICIDES IN PERSPECTIVE

A discussion paper regarding research on pesticide management for  
the cotton industry



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2<sup>nd</sup> Edition

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## PREFACE

The CRC for Sustainable Cotton Production (Cotton CRC) was established in 1993 to develop and implement management practices to ensure the sustainability of the cotton industry. Identified as a priority among the research programs was that of Protecting the Resource Base and the Environment. Since the cotton industry was perceived to have a heavy reliance on pesticides, a subprogram on Environmental Protection (Pesticides) was established to address an area of particular importance. Later, the Cotton CRC was refunded to 2006 as the Australian Cotton CRC. Research and extension efforts directed at reducing reliance on pesticides and their impacts on the environment remain a high priority.

This discussion paper attempts to place the issues associated with pesticide usage in perspective. From the results of several research projects on crop protection chemicals, related to their environmental fate and transport, their containment on cotton farms and remediation of soil and water. The discussion paper demonstrates how research outcomes can help prevent problems. Had the approaches now recommended in this paper been in place for all chemicals used in the past, some acute crises might have been avoided or their effects minimised.

The paper focuses on research establishing the physical, chemical and biological properties of chemicals needed for cotton production. It provides protocols for field monitoring of chemicals and methods for their remediation. This information, through collaborative work with LWRRDC and the CRDC, has already been integrated into cotton industry's Best Management Practices guidelines. By understanding these chemicals we can develop improved practices by cotton farmers and help provide a perspective that brings environmental benefits to the cotton industry and to society as a whole. Widespread adoption of all elements of BMP will add significantly to this goal.

The introduction of transgenic cotton in 1996 has led to a substantial reduction in the quantity of chemical insecticides, particularly endosulfan, that need to be applied to the cotton crop. Improved transgenic cottons offer prospects for further reduction in pesticide requirement. Nonetheless a need for some insecticides and herbicides will remain. We are continuing our research effort to further minimise pesticide inputs, to conduct relative ecological risk assessment from different chemicals and to provide better choices for cotton farmers in farm management through the provision of integrated approaches for pest, weed and disease management.

The information provided in the *Cotton Pesticides in Perspective* database will be valuable to researchers, consultants and growers seeking comprehensive information about cotton pesticides and their environmental attributes. The recommendations contained in *Cotton Pesticides in Perspective* should help provide continued improvements in the responsible use of crop protection chemicals in the future.

Gary Fitt  
Director, Australian Cotton CRC

August, 2000

## CONTENTS

	page
PREFACE .....	5
INTRODUCTION .....	9
PESTICIDES AND THE AUSTRALIAN COTTON INDUSTRY .....	12
COTTON CRC RESEARCH PROJECTS .....	16
Spatial distribution of chemicals and the potential for transport off-farm (Project SU 1.1.1) .....	16
Containment of potential chemical contaminants (Project SU 1.1.2) .....	17
Bioremediation (Project SU 1.1.3) .....	17
Development of standard environmental tests for herbicides needed in cotton production (Project SU 1.1.5) .....	18
The CRC's research in relation to the LWRRDC/CRDC/MDBC Joint Program .....	18
RESEARCH RESULTS AND DISCUSSION	
<b>Spatial distribution and the potential for transport</b> .....	20
Transport of pesticides .....	21
<i>Drift</i> .....	21
<i>Volatilisation and transport on dust</i> .....	21
<i>Transport in surface runoff</i> .....	24
<i>Mobility and leaching to groundwater</i> .....	28
Degradation of pesticides in cotton production systems .....	29
<i>Chemical degradation</i> .....	30
<i>Photodegradation</i> .....	32
<i>Biological degradation</i> .....	33
Persistence .....	34
<i>Half-life of a chemical</i> .....	34
<i>Sorption to soil</i> .....	36
<i>With-holding periods</i> .....	37
Monitoring of residues - Immunoassays .....	37
<b>Containment of chemicals</b> .....	39
Adsorptive remediation of runoff from cotton farms .....	39
Sediment traps and flocculation to prevent transport of pesticides in runoff .....	40
Containment in gravel/soil filters using biofilms .....	41
<b>Bioremediation</b> .....	41
<i>In situ</i> bioremediation of soils .....	41
<b>Risk assessment</b> .....	43
Impacts on the environment .....	43
Modelling the distribution of chemicals using fugacity .....	44
Framework for ecological risk assessment (ERA) .....	45
<i>Relative risk to ecosystems</i> .....	46
Implications for farm management .....	47
<b>Conclusion</b> .....	48

<b>BEST MANAGEMENT PRACTICES</b>	
Recommendations .....	50
<i>Develop strategies to minimise the pesticide load on cotton fields</i> .....	50
<i>Containing pesticide residues on farm</i> .....	50
<b>LEGAL REQUIREMENTS</b> .....	52
<b>THE FUTURE</b>	
Industry directions .....	53
<i>The impact of transgenic (Bt) cotton</i> .....	53
<i>Herbicide-resistant cotton</i> .....	54
<i>Integrated Pest Management (IPM)</i> .....	54
Research directions .....	55
<i>Remediation of pesticide residues</i> .....	56
<i>Modelling to prevent risks</i> .....	56
<i>New monitoring tools</i> .....	57
<b>REFERENCES</b> .....	58
<b>APPENDICES:</b>	
1    Cotton pesticides and their application rates .....	66
2    Degradation processes for cotton pesticides .....	69
3    Field half-lives of cotton pesticides .....	71
4    Sorption and mobility of cotton pesticides .....	73

## INTRODUCTION<sup>1</sup>

Without pest control, food and fibre production and environmental health in Australia would be seriously threatened. World-wide, research data show that, without effective pest management, pre-harvest crop losses would average about 40 per cent. Australia is no exception - if insects, diseases and weeds could not be controlled, production of many field and horticultural crops simply would not be economical. Nor is pest control solely an agricultural concern - it has many other rural, urban and industrial applications. The fact is that, if pests could not be controlled, food and fibre production and environmental and human health in Australia would all be seriously threatened.

Given the massive publicity directed toward the use of chemical pesticides, it is no wonder that it is commonly thought that all pest management programs depend entirely on chemical use. Nothing could be further from the truth. In fact, non-chemical techniques, such as sanitation, cultivation, crop rotation, resistant cultivars, and biological control are widely and successfully used for pest control; chemicals are used primarily as a last line of defence. Because many pests cannot be controlled adequately without some chemical use.

***Non-chemical techniques are widely and successfully used for pest control; chemicals are the last line of defence***

The value of chemicals was recognised early in the development of agriculture. Inorganic pesticides such as sulfur and the arsenical and mercurial compounds and botanical insecticides such as pyrethrums - although only moderately effective - nevertheless represented an important advance in pest control.

But the development of DDT, 2,4-D and other synthetic organic pesticides around 1950 introduced a new era of pest management. For the first time, farmers could achieve excellent control of insects, weeds and plant diseases. It was even thought that, if applied in sufficient amounts, these chemicals would eliminate most pest species. This was not to be the case.

## RESISTANCE

Pests, particularly insects, showed great capacity to develop resistance. Today, world-wide, more than 700 species of insects, including many in Australia, are resistant to insecticides; plant pathogens resistant to fungicides are widespread; weed resistance to herbicides is becoming common.

Widespread use of these first organic pesticides, particularly DDT and other organochlorine (OC) insecticides such as dieldrin and heptachlor led to another unforeseen problem - they were persistent and bioaccumulated. This presented a potential residue problem in food, while from an environmental point-of-view, reproduction in fish and birds was affected.

It soon became clear that intensive use of these chemicals could no longer be tolerated and, in most developed countries, the persistent OCs were phased out. New chemicals, such as organophosphates, carbamates and pyrethroids were developed which were generally applied at lower rates and which did not bioaccumulate. But being less persistent, it often was necessary to apply them more frequently. Due to sustained use, many pests are now becoming resistant to some of these pesticides.

It was obvious that chemical-based pest management programs could not be maintained and that, in future, acceptable levels of pest control would be achieved only through better combination of chemical and non-chemical management techniques. Recently, many advances have been made in

<sup>1</sup> This is an edited version of text from the article 'Pesticides in perspective' published in *The Cotton Yearbook 1996*. The Australian Cottongrower, pp. 96-102.

developing these integrated pest management techniques - particularly for insect control.

Australian scientists have been in the forefront of some of this research, developing integrated programs for management of insecticide resistant pests (Forrester, 1990) and non-chemical methods of pest control.

Experience with the persistent OC insecticides demonstrated the fallacy of assuming that pest control agents could be developed and introduced without considering potential side-effects. Establishment of international standards for pesticide residues in agricultural produce and environmental concern with pesticide use forced governments, including those in Australia, to establish agencies monitoring and regulating pesticide use. In most developed countries, research on pesticide behaviour and environmental impact quickly became an important component of developing pest management programs.

#### THE COTTON INDUSTRY AND PESTICIDES

Without effective management programs, losses caused by pests - particularly insects - would be so devastating that cotton production would not be economical. For entomologists attempting to cope with managing insecticide resistant strains of insect pests, while losing effective chemicals one after another because of environmental concerns, it has been a constant struggle.

Nevertheless, effective management programs have been developed - more recently using a wider selection of less persistent insecticides from different chemical groups. But current cotton pest management programs still rely heavily on chemical use. It was not until 1995 that IPM recommendations promoted thresholds in addition to chemical group rotation.

***The need for research on the behaviour of pesticides***

Unfortunately, in Australia, while pest management research flourished, less emphasis was placed on pesticide

management research. This led to a number of problems, particularly the occurrence of pesticide residues in livestock and contamination of river systems.

But, to their credit, cotton growers and irrigation water users have financially supported monitoring programs of the riverine system by the NSW Department of Water Resources (Land and Water Conservation) and CRDC research on the fate of pesticides since about 1990. More recently, the scale of this research has been lifted including the development of the Cotton CRC and a number of programs are now in progress to investigate the movement of chemicals off farm, the behaviour of pesticides in the environment and accumulation and persistence in livestock and fodder.

It is essential that this research should continue after the current problems are overcome. Just as chemicals vary in effectiveness against different pests, so also do they vary in their persistence and behaviour in the environment - a fact which always should be taken into consideration. **Persistence and behaviour can only be established by appropriate research in pesticide management**, preferably as part of the registration process for new chemicals.

#### MANAGING PESTICIDE USE IN COTTON

***Conventional insecticide use will be reduced by 50 per cent by 2000***

In managing pesticide use, there are three logical steps:

- Minimise pesticide input;
- Contain the pesticide at the application site; and,
- Select for use pesticides with minimal environmental impact.



Reduction of pesticide use has been the goal of scientists concerned with insect control on cotton for many years, because it is important in terms of managing insecticide resistant pests. Through development of insect monitoring programs, economic thresholds and other techniques, substantial progress has been made. Introduction of *Bt* (Ingard®) cotton could result in a marked reduction in insecticide use. The aim of these programs was to reduce conventional insecticide use at least 50 per cent by the year 2000. Although such figure has been achieved on genetically modified cotton, its relative small contribution to the national cropping area means an effective 5 per cent net reduction. There is still some work to do to achieve that target.

***Chemicals will continue to have an important role in cotton pest management***

Although insecticide use should decline over the next few years, it is wrong to assume that environmental concerns will disappear. Insecticides will still be required to control some insect pests and, in the absence of frequent endosulfan applications, secondary pest populations may increase.

Herbicides will continue to be used for weed control. We need to ensure that harmful residues do not increase by proper selection of chemicals with shorter half lives as growers adopt reduced tillage techniques or as herbicide tolerant cotton varieties are introduced.

So even though total pesticide use may be reduced, the possibility that chemicals will continue to contaminate the environment will remain a concern. Attention will have to be directed toward developing ways to contain the residues to the greatest extent possible. And we have to ensure that where “leakage” does occur - perhaps as a result of drift or runoff during heavy rainfall - the pesticides used will have little environmental impact.

#### THE DISCUSSION PAPER

The material in this discussion paper is arranged as follows:

- A background section on the significance of pesticides in the Australian cotton industry includes information on estimated usage and draws attention to the industry’s consciousness of environmental issues that this usage raises.
- This is followed by a section that provides an outline of the Cotton CRC’s research program on pesticides and the expected outcomes of this research when it was undertaken. Links with other research and monitoring programs are indicated.
- In an extended section on research results, the range and usefulness of data obtained in field and laboratory is indicated. For example, in the case of data obtained for endosulfan, it is possible to draw up a chemical balance for its dissipation involving disparate processes such as drift, volatilisation, biological transformations and transport in runoff water from irrigations and storms and binding to sediments. The utility of new methods of immunoanalysis of pesticides, developed in the CRC’s research for field monitoring, is indicated. In addition, attention is drawn to a range of possibilities for containment of pesticides on cotton farms and for the remediation by processes carried out by plant and microbial systems. Finally, risk assessment methods are described.
- From these and other data, it was possible to indicate desirable farm practices, as they were later included in the Australian Cotton Industry Best Management Practices Manual. A brief account of the legal requirements for pesticide application is also included.
- In the context of current industry directions, gaps in research data are then discussed and recommendations for future action are given.

## PESTICIDES AND THE AUSTRALIAN COTTON INDUSTRY

The cotton industry is one of the largest users of chemicals in the Australian agricultural sector. These chemicals are used for insect control, weed control, protection of the crop against diseases, to foster productivity and facilitate harvesting, with pesticides being a major proportion of all chemicals used (CIE and Cameron, 1995).

The challenge for the industry is to cope with the public demand for clean and safer agricultural practices, reducing the environmental damage of excessive pesticide use while maintaining profitability. Negative public perceptions may lead to unwarranted changes in regulations detrimental to the industry. Further restrictions on the use of certain chemicals, for instance endosulfan, would leave the cotton industry in a vulnerable position to other undesirable outcomes such as loss of profitability and negative environmental impacts from alternative chemicals.

At present, a co-ordinated effort between growers and researchers is needed to ensure that the Australian cotton industry implements an environmentally friendly management plan that aims to reduce the usage of chemicals. This will bring a reduction in the costs associated with crop production and less impact on the environment. It is difficult to obtain accurate figures for the total quantities of pesticides used by the cotton growers, and the figures of Table 1 are only estimates for the most commonly used insecticides, herbicides (Charles *et al.*, 1995) and defoliants for the year 1991, when 260,000 ha were cultivated to cotton. More accurate figures are compiled by cotton consultants but these are not readily available for public use. It should be noted that endosulfan and pyrethroids account for 70% of all insecticides applied, or 80% of those used against heliothis (Cox & Forrester, 1992).

According to the Cotton Comparative Analysis of 1992/93 (Anon, 1994), pesticides and their application costs account for 20.5% of the total crop production expenses, totalling over \$96 million a year, or the equivalent of \$370 per hectare. On top of this figure must be added the cost of professional consultants (\$9 million in 1991). Table 2 shows the share of each type of chemical in the total expenditure, including fertilizers for comparison. Chemical usage makes up approximately 30% of total crop production costs. These figures are reduced by 40-50% in crops using Ingard<sup>®</sup> cotton (Pyke, 1999).

**Table 1. Estimate of cotton pesticide usage in Australia, 1991**

Product name	Total litres (thousands)	Litres/ha
<b>Insecticides*</b>		
Endosulfan	4,828	18.5
Pyrethroids	1,651	6.4
Profenofos	910	3.5
Chlorfluazuron	650	2.5
Dimethoate	520	2.0
<i>B.thuringiensis</i>	390	1.5
Methomyl	260	1.0
Thiodicarb	130	0.5
<b>Herbicides**</b>		
Diuron	602	2.3
Trifluralin	449	1.7
Fluometuron	385	1.5
Pendimethalin	184	0.7
Prometryn	161	0.6
Glyphosate	101	0.4
Atrazine	86	0.3
Metolachlor	24	0.1
<b>Defoliants</b>		
Ethephon	520	2.0
Thidiazuron	24	0.1

\* Estimate of total endosulfan and synthetic pyrethroid usage, at 3.0 L/ha. Source: Hoechst Australia Limited, cited in Barrett, Peterson and Batley, (1991)

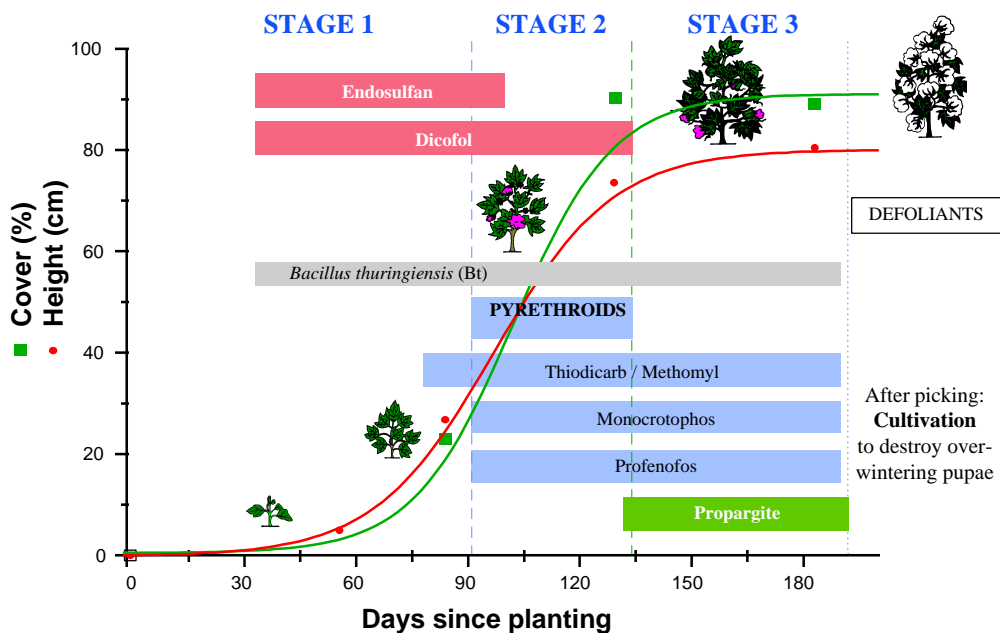
\*\* Adapted from Buster (1994)

**Table 2. Cost of chemicals and pesticides used by the cotton industry**

	Total Australia 91/92 (millions of \$)	Total cost/ha (\$)	%production cost
Insecticides	44.6	171.5	9.5
Herbicides	21.5	82.7	4.6
Defoliants	12.6	48.5	2.6
<i>Subtotal pesticides</i>	<i>78.7</i>	<i>302.7</i>	<i>16.7</i>
Application costs	17.8	68.5	3.8
Consultants	9.0	34.6	1.9
<b>TOTAL PESTICIDES</b>	<b>105.5</b>	<b>405.8</b>	<b>22.4</b>
Fertilizers	35.1	135.0	7.2
<b>TOTAL CHEMICALS</b>	<b>140.6</b>	<b>540.8</b>	<b>29.6</b>

The number of sprays applied to a crop varies with the location and the season, with a national average of 11 sprayings per season for insecticides, and 3 applications for herbicides in 1998/99. For Ingard<sup>®</sup> cotton, however, an average reduction of 5.4 sprays (37%) was achieved in the same season. New management practices for heliothis control are favouring cultivation, and therefore a reduction on herbicide usage is expected.

The dependence on pesticides has led to serious problems for the industry. The main problem arises from excessive usage in order to keep the cotton crops free of pests, with the resistance and environmental problems which it brings. While some growers tolerate a degree of damage to their crops by using as little pesticide as possible, others prefer to use more to ensure there is no pest damage. The latter approach poses an obstacle to the insect resistance management strategy (IRM), implemented in 1984 in response to the increased resistance to synthetic pyrethroids the previous year (Forrester, *et al.*, 1993; Fitt, 1994; Fig. 1), and accentuates environmental risks.



**Figure 1. Insect Resistance Management strategy for the Macquarie Valley**

Although the significant use of chemicals is essential for the cotton industry, they are acknowledged as potentially harmful to the environment. Aware of its responsibilities, the industry has promoted several programs aimed at minimising the use of chemicals, thus reducing the negative effects on the environment.

The steps towards achieving this goal have been undertaken through the following programs:

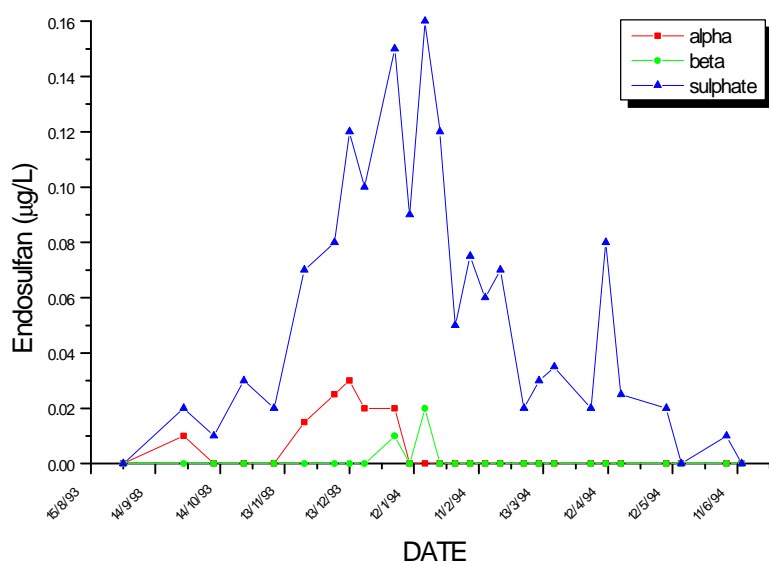
- an independent environmental audit, by Gibb Environmental Sciences and Arbour International, concluded in 1991
- a water quality monitoring program, conducted since 1991 by the NSW Department of Water Resources
- research to study the impact of pesticides on the riverine environment, mainly by the CRC for Sustainable Cotton Production, and the Land and Water Resources Research & Development Corporation (LWRRDC), with the Cotton Research and Development Corporation (CRDC) and the Murray Darling Basin Commission (MDBC)
- management, by co-ordinated efforts of several groups and organizations within the industry

The water quality monitoring program provides baseline data against which trends can be measured. As shown in Figure 2, there was significant contamination of rivers by endosulfan associated with the spraying season for 1993/94. Studies of this kind conducted by the NSW Department of Land and Water Conservation (DLWC) and financed by a voluntary levy on water users, provide a baseline against which future improvements in pesticide use can be assessed.

Maximum pesticide residue levels in river waters are established by the ANZECC Water Quality guidelines and the NHMRC/ARMCANZ Australian Drinking Water guidelines. A summary of levels for insecticide and herbicides used in cotton production is in Table 3.

In the remainder of this paper, we will address the main issues concerned with the environmental fate of pesticides, discussing previous and current research data to propose future terms of reference for research in this field. The Cotton CRC's research program on pesticides provides a sound scientific platform for discussion of issues relating to chemical usage and contamination to the environment. The results of the program will be used for developing management plans for the various outcomes, but it will ultimately be the responsibility of the cotton industry to implement them and therefore sound, cost-effective recommendations are essential.

Central and North-Western Regions Quality Program 1993/94



**Figure 2. Endosulfan contamination in the Macquarie Valley (After data from Cooper, 1994)**

**Table 3. Environmental, water quality guidelines and pesticide concentrations in river water**  
 (After Cooper, 1996)

	1992 ANZECC Water Quality Guidelines(mg/L)	1996 NHMRC/ARMCANZ Australian Drinking Water Guidelines (mg/L)	Concentrations found in river waters (mg/L)
<b><i>Insecticides</i></b>			
Endosulfan	0.01	0.05	0.1 - 0.6
Profenofos	n.a	0.3	<0.1
Parathion	0.004	10	<0.1
Chlorpyrifos	0.001	n.a.	0.1 - 8.7
<b><i>Herbicides</i></b>			
Atrazine	n.a.	0.5	0.1 - 2.0
Glyphosate	n.a.	10	-
Diuron	n.a.	n.a.	0.1 - 4.5
Fluometuron	n.a.	n.a.	<0.1
Metolachlor	n.a.	2	<0.1
Prometryn	n.a.	n.a.	0.1 - 1.2
Pendimethalin	n.a.	n.a.	<0.1
Trifluralin	n.a.	0.1	<0.1

n.a. Not applicable

## COTTON CRC RESEARCH PROJECTS

The Cotton CRC has funded research on environmental protection from the effects of pesticides in sub-program 1.1 since 1993. This sub-program was designed to cover four main project areas that had been given high priority. These areas were:

### 1. Spatial distribution of chemicals and the potential for transport off-farm (Project SU 1.1.1)

A CRDC-funded study on the environmental fate of endosulfan sprayed on cotton for insect control (see Kimber *et al.*, 1994) provided the baseline for further CRC studies on the fate and transport of pesticides applied to cotton farms. As a major project in the sub-program, three studies were proposed to achieve the following aims:

- (i) to establish the current burden and seasonal profiles of chemicals in cotton-growing soils, contaminated water, cotton plants, their mechanisms and rate of dissipation, and the extent of their transport to the riverine environment;
- (ii) to develop test kits (immunoassays) for pesticides used in growing cotton, for use in the field and to assist in decision-making regarding residues; and
- (iii) to provide an accessible database on practical protective measures for chemicals.

(i) *Environmental fate and dissipation studies.* It was intended to study selected farm chemicals considered to be of environmental concern, commencing with endosulfan and lambda-cyhalothrin. Following these studies, several other insecticides such as pyrethroids and the chitin synthesis inhibitors chlorfluazuron and lufenuron (benzoylphenylureas) were to be included.

Basic research on dissipation rates and mechanisms of degradation of insecticides in soil, foliage, and water runoff was carried out in an effort to determine the relative significance of different processes involved, ranging from volatilization, chemical and photochemical degradation, to biodegradation in soil and water runoff. This work was done as part of the LWRRDC/CRDC/MDBC program on "Minimising the Impact of Pesticides on the Riverine Environment using the Cotton Industry as a Model".

Studies at Auscott Narrabri and Warren in three seasons, from 1993 to 1996, established detailed chemical balances for endosulfan applied to cotton fields, indicating the significance of transport by volatilization (mainly of the alpha-isomer), conversion on-field to endosulfan sulphate and retention in soil, degradation by hydrolysis to the diol form, and transport of residues in runoff. In the 1995/96 season, degradation rates in ponded runoff and in farm channels and water-retaining areas were studied, with particular attention being paid to sediments. These studies yielded important information regarding half-lives of endosulfan in soil and water, allowing recommendations about safeguards in releasing runoff water following storms.

At the completion of this study, a full report was submitted to LWRRDC (Kennedy *et al.*, 1997), a summary of which was published in the proceedings of a national conference in Canberra (Kennedy *et al.*, 1998c). Publication of the results in the international Journal of Environmental Quality, and presentations to several national and international conferences complete the widespread diffusion of this research - see References section for full details.

(ii) *Immunoassays.* Validation of immunoassay kits for endosulfan - developed under a previous CRDC project conducted jointly between CSIRO Division of Plant Industry and the University of Sydney (Lee *et al.*, 1995) -, and the development of immunoassay kits for pyrethroids and several herbicides were the objectives of this second project. It was expected that endosulfan immunoas-

says together with other immunoassays available from CSIRO (diuron, DDE and DDT), could be used in associated research of the CRC and other future research programs. At present, new pesticide immunoassays continue to be developed under other programs funded by the GRDC.

(iii) *Farm chemicals database.* The preparation of a computer database on all chemicals used in cotton production was undertaken to assist other aspects of this research program. Initially, this database was prepared in Microsoft Access (PC) and FoxPro (Macintosh) programs. Later, a version in FileMaker Pro, for both the Macintosh and Windows operating systems, has also been provided. The Cotton Pesticides Database covers information on pesticides useful to both research workers and the cotton industry in general.

The computer database was first completed in 1997 and issued as a hard-copy of *Cotton Pesticides in Perspective*, volume 2. Yearly updates of the database, including both new and old chemicals, would be made available on CD-ROM. Its information has been used in the preparation of several lectures for the external studies program (Certificate in Rural Science, UNE) since 1994.

## 2. Containment of potential chemical contaminants (Project SU 1.1.2)

The aim of this second project was to develop buffering techniques to maximise the retention or breakdown of nutrients and pesticides on cotton farms and it was approached in three stages.

(i) *Studies on adsorptive remediation of runoff from cotton-farms.* In this phase of the project, a range of potential adsorbents were examined to determine their adsorption-desorption characteristics with respect to pesticides currently used for cotton growing, and potential new chemicals. These characteristics were determined using classical techniques.

Once the behaviour of particular pesticides is established on defined adsorbents, strategies for extending these findings to on-site containment could be developed, and so the study was to include materials such as straw, coal fines, pulverised cotton stalks and trash, and other available bulk media.

(ii) *Studies on sediment traps and flocculation methods to prevent transport of pesticides in runoff.* This phase of the work consists of a trial on the use of polyacrylamide (PAM) as a flocculant on cotton fields to prevent sediment transport.

(iii) *Containment in gravel/soil filters using biofilms.* This approach to pesticide retention involves laboratory study of the potential use of filtration beds for runoff supplied with microbial biofilms. The technique has been tested using atrazine-degrading microbes that were isolated after perfusion of a grey-cracking clay for three years with a dilute solution of atrazine. This may be later extended to other pesticides and herbicides.

## 3. Bioremediation (Project SU 1.1.3)

The aim of this third project was to find microbes and/or microbial-plant systems capable of degrading pesticides, and two objectives were pursued:

(i) *To develop plant-microbial systems for accelerated pesticide degradation in cotton production.* Based in previous models for pesticide degradation (e.g. 2,4-D degradation in wheat, canola,

and clover plants associated with plasmid containing bacteria), the potential for similar systems to be developed on cotton production systems with wheat and appropriate summer legumes would be investigated.

(ii) *To test soil and water for plant-microbial systems capable of degrading pesticides in cotton production areas.* Laboratory and field trials in cotton growing fields will be conducted to test for bioremediation. These will be based on the plant-microbial systems developed above and on another system based on cyanobacteria, which has shown degrading capabilities in the laboratory.

#### **4. Development of standard environmental test for herbicides needed in cotton production (Project SU 1.1.5)**

Studies on herbicides commenced in 1997 following the appointment of a post-doctoral fellow. The aims of this research were:

- (i) to examine the fate and transport of herbicides in cotton growing soils;
- (ii) to characterise the risk of herbicides used in cotton production and provide information that can help growers select herbicides that will have minimum impact on the environment.

(i) *Fate and transport of herbicides.* Using laboratory experiments, the key physico-chemical properties of four herbicides (solubility in water and octanol, vapour pressure and bio concentration factor) in three different cotton growing soils (a black soil from Narrabri; a brown soil from Moree and a red soil from Wee Waa) were determined. The sorption experiments provided kinetics and equilibrium values for sorption ( $K_d$ ) and partitioning to organic carbon ( $K_{oc}$ ) of herbicides. The persistence of those herbicides for varied soil moisture and temperature regimes under laboratory conditions was also determined, and the corresponding half-lives were calculated. A similar study under field conditions to validate the laboratory results is still under way and expected to be finished by June 30, 2000. The results of the laboratory work have been published in international journals (e.g. Baskaran and Kennedy, 1999), and both laboratory and field results will be incorporated in the risk assessment process.

(ii) *Risk characterisation of herbicides.* The above tests have provided new data for the development of parameters and risk factors in particular cotton growing environments. Significant progress has been made in the risk assessment process, which integrates several sources of information (research input data and cotton pesticide database) together with predictive models (fugacity model) to estimate the risk of any herbicide in cotton agro-ecosystems. A relative risk rating of each herbicide under specific growing conditions can be determined using the newly developed EcoRR scoring method (Sánchez-Bayo *et al.*, 2000), which provides a tool that enables cotton growers to choose the chemicals of lesser risk to the environment. This and other outcomes of the project will be extended through the CRC to the Cotton industry.

#### **The CRC's research in relation to the LWRRDC/CRDC/MDBC joint program**

In 1993 a major research program involving the Cotton CRC Subprogram 1.1 was undertaken with the title: *Minimising the Impact of Pesticides on the Riverine Environment Using the Cotton Industry as a Model*. The research funding groups involved the Land and Water Resources Research and Development Corporation (LWRRDC), the Cotton Research and Development Corporation (CRDC),



and the Murray Darling Basin Commission (MDBC), with infrastructure support from the CRC for Sustainable Cotton Production. Program goals were to

- determine the transport and fate of pesticides applied to cotton;
- assess the impact, if any, of current pesticide use on the rivers;
- develop practical and economic methods to minimise the transport of pesticides from application sites; and,
- provide a sound scientific basis for development of management guidelines and regulatory codes.

Research team members, drawn from the Universities of Queensland and Sydney, University of Technology Sydney, Griffith University, Queensland Department of Primary Industries in Brisbane, Toowoomba and Emerald, New South Wales Department of Agriculture at the BCRI, Rydalmere, the Department of Land and Water Conservation and CSIRO quickly pulled together a cooperative research effort in which rapid progress has been made.

Equipment for measuring aerial transport (drift, volatilisation, dust) and surface runoff was provided and tested, as in the case of the rain simulator. Procedures for sampling air, water, soil and sediment were devised and studies on the impact of pesticides on aquatic organisms were established. New techniques for analysing insecticides (immunoassays) thought to be of concern were developed in the CRC for Sustainable Cotton Production as mentioned above, and were also applied in this research program.

Participation in this Joint Program has significantly increased the scale of research that was possible in the CRC, particularly in the case of the insecticide endosulfan. The research data obtained was expected to provide a model of how other chemicals may behave in the cotton environment. The results were presented at the 1998 Pesticide Conference in Canberra, and its proceedings published as a LWRRDC Occasional Paper 23/98 (see References section). Currently, part of this research is being printed in a special issue of the international Journal of Environmental Quality due to appear by the end of 2000. As a result of this team effort, a manual for best management practices in the Australian cotton industry was developed (Williams, 1998).

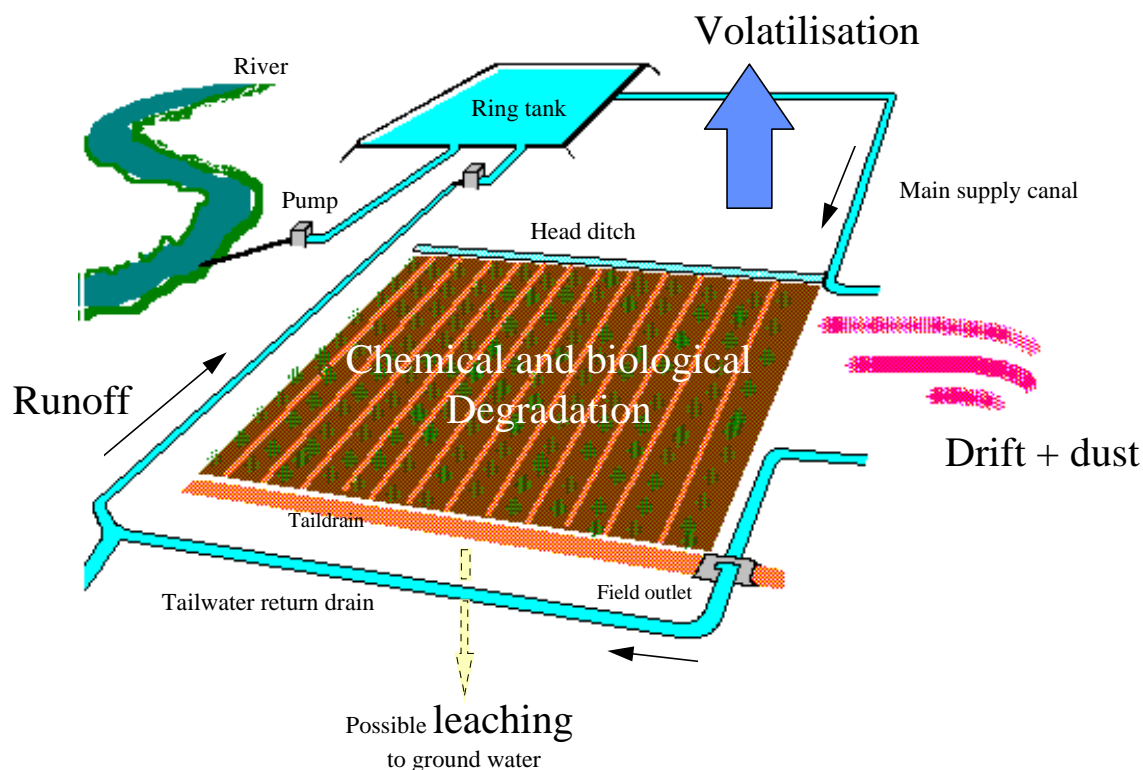
## RESEARCH RESULTS AND DISCUSSION

### Spatial distribution and the potential for transport

The fate of pesticides and other chemicals applied on cotton farms depends on many factors. In general, dissipation of farm chemicals can occur by transport processes such as drift, evaporation (volatilisation), washing off in surface water (run-off), percolation into deeper soil leading to leaching into groundwater, or by chemical, photolytic and biological degradation (biodegradation) processes that break down the chemicals (Fig. 3).

In particular, the physical and chemical properties of a pesticide will greatly determine its behaviour in the environment. For instance, water soluble chemicals will tend to move into surface and ground waters, whereas volatile chemicals will dissipate mainly by evaporation on field. Other properties will determine whether a particular chemical will dissipate or will remain bound to the soil, sediment or plants. These and other properties will influence the likelihood of breakdown by physico-chemical processes, or by biodegradation in plants and microbes present in the soil or water. In addition, the rates of dissipation and degradation will be affected by a complex of environmental factors, including temperature, moisture and pH in soil, wind conditions, etc.

Therefore, knowledge of the pesticide's properties and the ecological factors that control their fate in the environment is very important, since it will form the basis for sound farm practices. The following pages are an attempt to describe the processes determining the fate of chemicals in the environment, and are illustrated with data obtained during our research. In doing this, processes



**Figure 3. Dissipation pathways of pesticides in irrigated cotton farms**

have been considered in two groups: 1) those affecting the transport of chemicals from the farm environment, and 2) those relating to the persistence of the chemical in soil or other environmental media.

## Transport of pesticides

### *Drift*

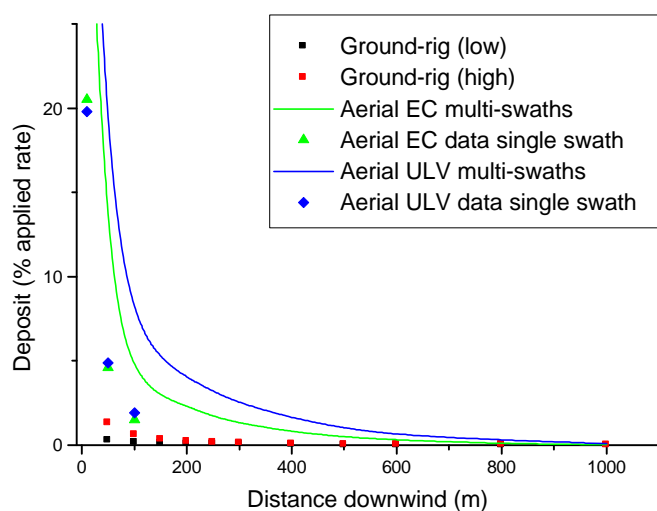
Wind acts as a major force for pesticide dispersal during and after the application of chemicals on field. At the time of application, wind can transport the chemical droplets hundreds of metres away from the crop, thus contaminating nearby land. After the chemical has settled, wind can induce a faster evaporation of pesticide from plants and soil and carry the vapour away. In addition, wind may move pesticide in dust particles from the top soil and disperses them over large areas.

The movement of droplets away from the crop being sprayed is independent of the physico-chemical properties of the pesticide, but depends on factors such as the application mode (aerial, ground-rig), formulation used (emulsifiable concentrate, EC or ultra-low-volume, ULV), the type of nozzles and most importantly the wind speed (Bird *et al.*, 1996). Safety directions for spraying have to be observed in order to guarantee that minimal contamination by drift occurs. The Centre for Pesticide Application and Safety (C-PAS) has published a handbook with indications about how to minimise the drift contamination from chemical sprayings on Australian farms (C-PAS, 1994). These include a number of regulations concerning the use of machinery, as well as indications of weather conditions suitable for application, especially in the case of aircraft spraying.

Studies on endosulfan applications on cotton fields have established that under recommended weather conditions, i.e. for wind speeds between 3 and 15 km/hr, drift of droplets was detected as far as 1.5 kilometres downwind from the aircraft, although most of the drifting pesticide falls in the first 100 metres (Fig. 4). Losses by drift are estimated at 5-10% of the total amount sprayed (Woods *et al.*, 1998a). For endosulfan drift onto pasture, residue concentrations may vary between 37-60 mg/kg at close distances (<100 m) and 2-3 mg/kg about 1500 m, sufficient to cause a contamination problem on cattle grazing near a cotton farm. Research to decide whether EC formulation may be preferable to ULV in reducing drift, because of larger droplet size, is currently being conducted (Woods *et al.*, 1998b). However, questions regarding efficacy must also be considered and substituting EC for ULV may not be desirable if more applications of EC are required. The possibility of better formulations is not explored in this paper.

### *Volatilisation and transport on dust*

Vapours and minute dust particles float in the airstream and may be carried over long distances in thermal updraughts. While droplet drift may be controlled by air turbulence and gravity, vapour drift is practically impossible to control. Endosulfan vapour and dust drift has also



**Figure 4. Drift of endosulfan from a cotton field**

been studied in a similar fashion by placing metal trays containing shallow water (5 cm depth) at several distances from the field of application (Edge *et al.*, 1998).

Contamination of the water by vapour alone was highest nearest the field, with concentrations around 0.01 µg/L at 200-400 metres, 48 hours after the spraying. These are basically the same levels as set by ANZECC in its environmental guidelines, but such shallow water is not relevant to water bodies like dams and rivers where considerable dilution occurs. Dust contamination was also highest closest to the field, as expected. However, dust collectors placed at the above distances showed that transport of endosulfan on dust particles blown away from the sprayed areas is a minor component of the overall contamination off-field.

Evaporation from soil, plant and water surfaces is a feature of some volatile pesticides. The ability to volatilise is related to the chemical structure and molecular weight of each compound, and it becomes relevant when considering the type of spray that should be used: small droplets such as ULV evaporate to tiny particles of concentrated pesticide. Volatile chemicals will result in drift as vapour, posing a hazard to the environment and representing a waste which should be minimised.

Volatility depends mainly on two physical properties: vapour pressure and solubility. Since water is the only solvent found in field situations, volatility of a chemical can be expressed as the ratio between its vapour pressure and its solubility in water (Henry's constant). Thus, the higher the vapour pressure and the lower the solubility, the more likely is volatilisation to occur. Figure 5 shows the solubility in water of many pesticides plotted against their vapour pressure at normal temperatures (20 °C). In general, herbicides tend to be less volatile than insecticides because of

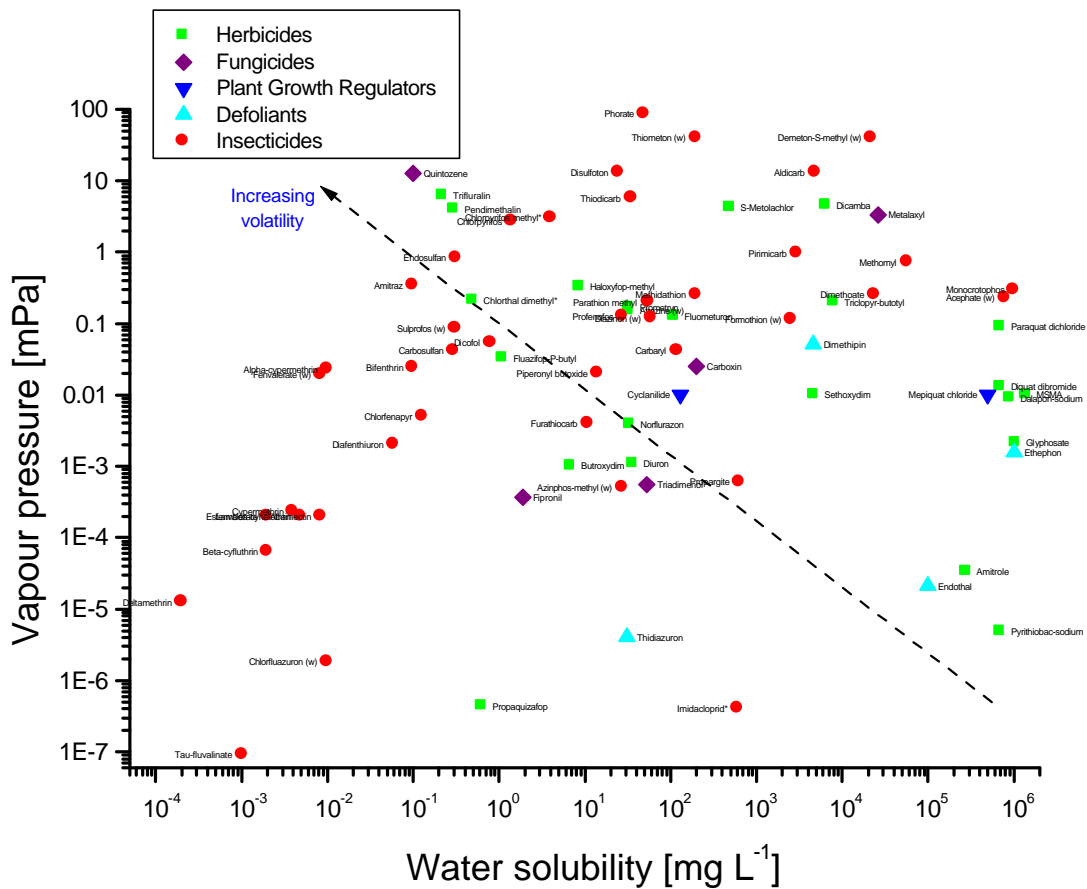


Figure 5. Volatilization as expressed by Henry's law ( $H = \text{vapour pressure} / \text{solubility}$ )

their greater solubility in water, but there are exceptions like trifluralin and pendimethalin, both of which are as volatile as the insecticides endosulfan or chlorpyrifos. Amongst the insecticides, pyrethroids are remarkably insoluble and at the same time not very volatile (bottom left in Fig. 4), when compared to organophosphates and endosulfan. This makes pyrethroids ideal chemicals for insect control and safe from an environmental point of view.

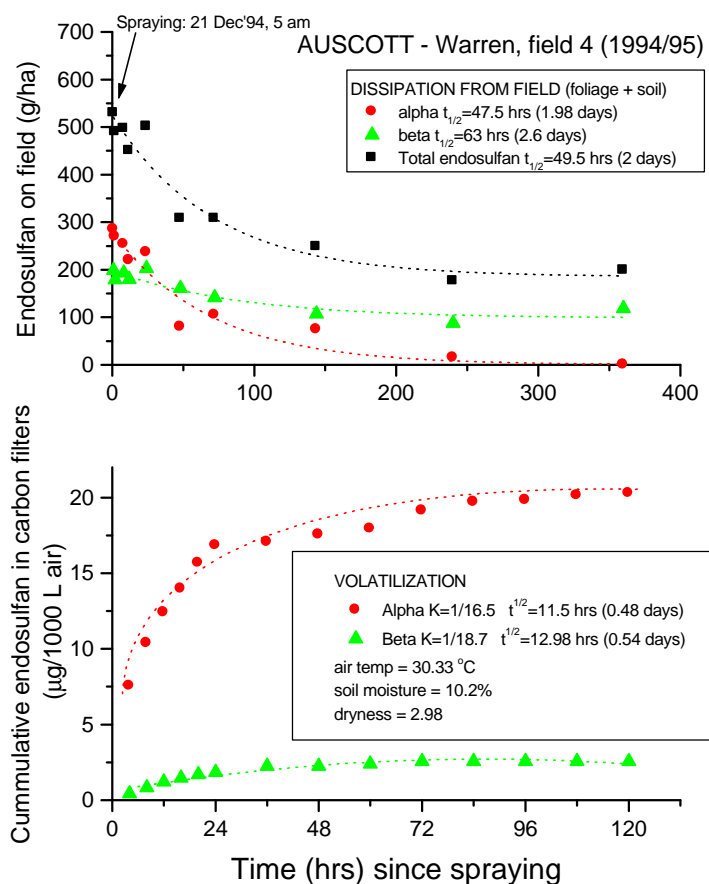
Other variables influencing the rate of volatilisation of a pesticide from field surfaces are:

- temperature
- concentration
- wind conditions
- relative humidity in air
- soil moisture
- organic matter and clay content in soil
- plant cover

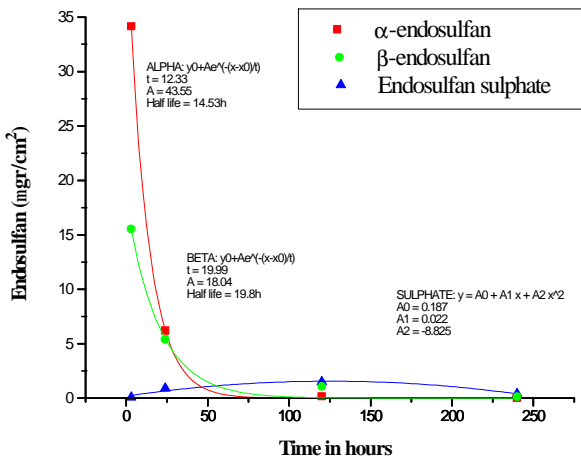
An increase in most of the variables listed above will increase volatilisation. However, the more organic matter content in soil and the greater the plant cover, the less evaporation will occur. Many studies have shown that increasing soil moisture also increases pesticide volatilisation, probably by hydration of possible binding sites on soil fractions.

Data from field studies using air pumps fitted with carbon filters that adsorb endosulfan vapour indicate that the alpha-isomer is the major volatile component in the first week after endosulfan application (Fig. 6), consistent with its almost complete disappearance within 200 hours. The total proportion of endosulfan that is volatilised from cotton fields can be as high as 65-90%. Additional research on the initial rate of dissipation of endosulfan when applied to the leaves of cotton plants in a glasshouse conditions showed rapid disappearance of the alpha- and beta-isomers (half-lives of less than 1 day and 3 days respectively) and very little conversion to endosulfan sulphate (Fig. 7). Similar results have been obtained from field trials, which found that 95% of the endosulfan applied disappears in two weeks from the cotton foliage (see Fig. 14).

Volatilisation, though it represents a net loss of pesticide applied, is considered unlikely to lead to serious contamination of nearby water. Concentrations of pesticide vapours in the air surrounding a cotton farm have not been measured, although



**Figure 6. Dissipation of endosulfan from a cotton field (top) and volatilisation of alpha- and beta-endosulfan (bottom).**



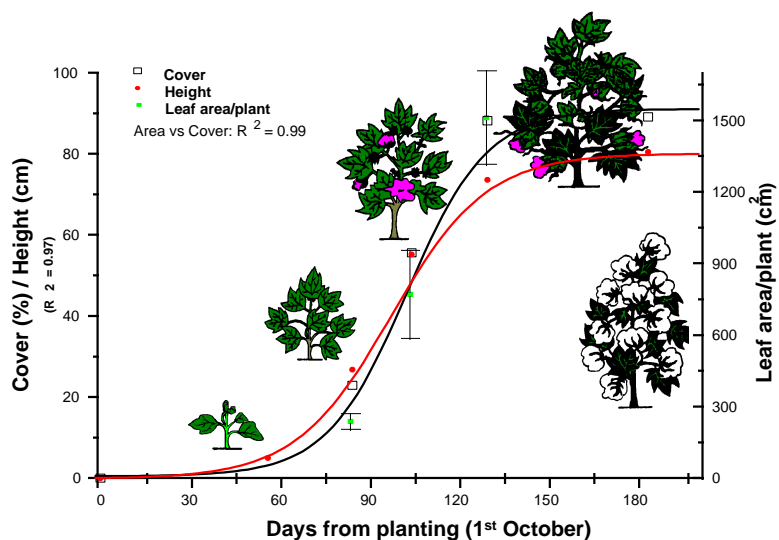
**Figure 7. Half-life of endosulfan in cotton leaves** (After Coleman, 1994)

they have been modelled for endosulfan (Raupach *et al.*, 1996). It seems possible that volatile insecticides can affect large areas around those targeted. This could also be damaging in the case of herbicides because of the harm they can cause to sensitive crops. For this reason 2,4-D herbicides as esters, which are very volatile, were excluded from being used by the cotton industry.

Water runoff, whether from irrigation or storm waters, is potentially a major cause of pesticide transport off the field. Because of their organic nature, most pesticides tend to bind to soil, specially to the organic matter and clay particles, and are mobilised whenever soil erosion occurs. Pesticides with low solubility in water will move with the sediment component during erosion, whereas soluble chemicals will travel mainly in the effluent water. With 92% of Australian cotton farms being routinely irrigated, it is clear that runoff is a major issue for controlling water contamination by farm chemicals. Raingrown cotton will also be subjected to water runoff during storms, so all growers must be aware of the possible hazards posed by irrigation or storm waters leaving the farm. Later in this publication some practical measures about reducing contamination in runoff, based on the findings of this research, will be discussed.

#### Storm wash-off and runoff

During rainfall, the extent of water runoff has been shown to depend on the extent of plant cover and current soil moisture content. Experiments with a rain simulator in cotton fields at Emerald, Queensland (Silburn *et al.*, 1995), have shown that after heavy rainfall (70 mm in 40 minutes) onto a dry soil, water runoff is negligible and soil loss is reduced to zero when plant cover is greater than 45-60%, depending on the soil compaction. This degree of cover is reached when most plants have blossomed in mid January (Fig. 8), and it can be expected that for most cotton crops no soil will be lost during isolated storms in mid-summer. However, early in the season, runoff would be substantial and could carry away as much as 2-3 tonnes of soil per hectare if cover is no greater than 10%, or about 1 tonne when cover is

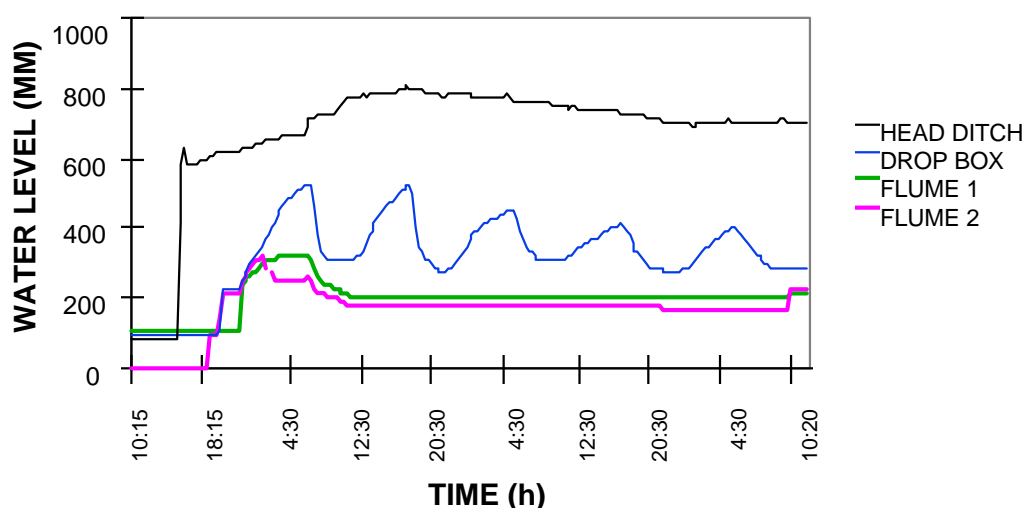


**Figure 8. Growth and plant cover of a cotton crop.**

25%. These findings highlight the need to contain water runoff from storms as far as possible, not only because of soil losses but also to reduce the pesticide contamination associated with this soil loss.

In the same experiments, it was shown the amount of pesticides in runoff depended on the water solubility characteristics of each chemical. For more soluble herbicides such as prometryn, higher concentrations were found in the runoff under any cover, whereas for less soluble insecticides such as endosulfan the total loss from the field was related to the total loss of soil, becoming negligible when no soil erosion was observed under a cover of 50% or more.

In mature crops with a high plant cover, a rain simulator study showed that the first flush of rain washes most of the endosulfan from the foliage of plants. For example, after an application of ULV endosulfan, its concentration on plants was halved by 5 minutes of rain, being almost entirely washed off after 25 mm of rainfall. Total quantity of endosulfan washed from plants declined rapidly with time since application: compared to the two hours, total wash-off was 29% after 1 day, 7% after 3 days and 1% after 8 days. This is due to the absorption of the pesticide by leaves. Twenty minutes after the rain started, runoff was first observed in furrow water. It was apparent that the endosulfan initially washed off the plants was partly absorbed by the soil, and so the water runoff on soil never carried as much pesticide as direct wash-off (Silburn *et al.*, 1996).



**Figure 9. Irrigation hydrograph in a cotton field**

### *Irrigation runoff*

If storm runoff is important in terms of soil erosion so is the irrigation runoff. The environmental effect of pesticide moving off during irrigation may not be considered as serious provided all sediment and runoff water is retained on farm. However, enrichment of pesticides in eroded sediments and transport of residues from the point of application are considered undesirable since they increase the risk of contamination off-farm (Ghadiri and Rose, 1993). Moreover, while storms are sporadic events, often not causing runoff, irrigations always imply runoff and percolation, washing the soil throughout most of the cotton growing season. In the majority of Australian cotton farms at any given time there is always at least one field being irrigated, usually at an average rate of 1 megalitre of water per hectare, with a total of 5 or 6 irrigations per season. During this time an array of different insecticides are sprayed on the crop and, if there is any opportunity for contaminated

water to enter the riverine ecosystem (without being adequately treated), the fears of environmentalists will be justified and there are bound to be repercussions to farmers.

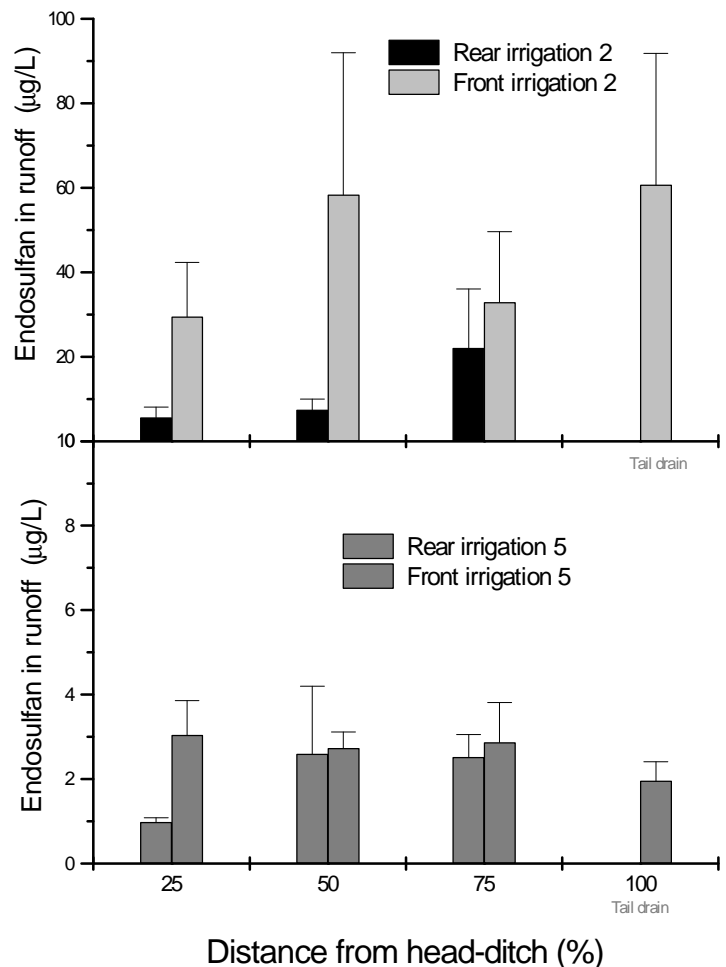
When a cotton field is irrigated, water is siphoned from the head ditch into the furrows. Water movement along the furrow is slow, on average about 100 metres per hour, the water seeping through the soil beds to moisten the subsoil and reaching the plant roots. The hydrograph shown in Figure 9 indicates uncalibrated stage heights at the head ditch, in two flumes placed in furrows and the outlet (drop-box). The cyclical nature of the hydrograph at the outlet resulted from progressive changes in the set of siphons, so that sampling hydrograph at the outlet could be considered as replicated five times. Stubble on field drastically curtails runoff and erosion, whereas loose or cultivated topsoil is more prone to erosion. We have observed, in our studies at Warren, that the water in the advance front carries debris (stubble, trash, etc) from the bottom of the furrow, with furrows having large amounts of debris substantially slowing water flow.

*Pesticide movement along the furrows*

Measurements of endosulfan concentrations in water runoff at fixed points along the furrow have shown that:

- 1) the advance front can carry as much as a five-fold higher amount of pesticide than the water behind;
- 2) sediment loads in the advance front were higher than in the water behind;
- 3) about 80-85% of the endosulfan was found in the water fraction of the irrigation runoff, with the remaining 15-20% being carried in the sediment load;
- 4) there was no evidence of a continuous pesticide build-up as the water moved along the furrow, but its concentration varied from one point to another in the same furrow, suggesting that other factors such as binding and desorption from soil, infiltration, flow dynamics, etc, caused irregularities in the measured concentrations (Fig. 10).

The absolute endosulfan concentrations measured in runoff in furrows varied from a high value of 45 µg/L early in the season (mid-December) to a low of 2.6 µg/L in later irrigations (mid February). The concentration in water runoff reflects the pesticide load in soil at the moment



**Figure 10. Endosulfan loadings along furrows during two irrigations at field 20 [Auscott Warren, 1995/96]**



the field is irrigated, which is more heavily contaminated after the first sprayings in December, when there is low plant cover, than later in the season (Kennedy *et al.*, 1997). Most of the endosulfan present in water runoff early in the season is of the formulation type, i.e. alpha and beta isomers, whereas in the late irrigations the form of endosulfan found is mainly the sulphate, a form produced by soil microorganisms (Guerin and Kennedy, 1991), collembola (Park, 2000) and foliage.

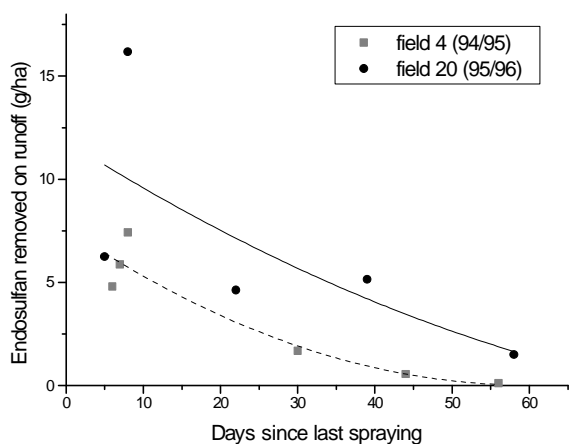
The irrigation waters reach the end of the field and move along the taildrain until they are discharged through an appropriate outlet into a collective return drain. Some sediment from the furrows is deposited in the taildrain but the remainder goes off-field through the outlet. The amount of sediment carried in the water of taildrains depends on the slope (Simpson *et al.*, 1995), soil type, soil moisture at the time of irrigation, and amounts of water being discharged, and therefore varies considerably from field to field. In general, soil in the taildrain does not differ from field soil in terms of pesticide concentration (Table 4). Sampling of soil at the taildrain two and a half weeks after the final spraying in the season showed that the concentration of endosulfan on taildrain deposits was much the same as in the field soil.

**Table 4. Endosulfan concentration (mg/kg) in topsoil (0-5 cm)**

Days after spraying	On field	Taildrain
0	0.80	1.02
1	0.86	0.51
2	0.49	1.35
5	0.35	0.56
6	0.39	0.22
17	0.39	0.32
205	0.10	0.10

*Pesticide load in runoff leaving the field*

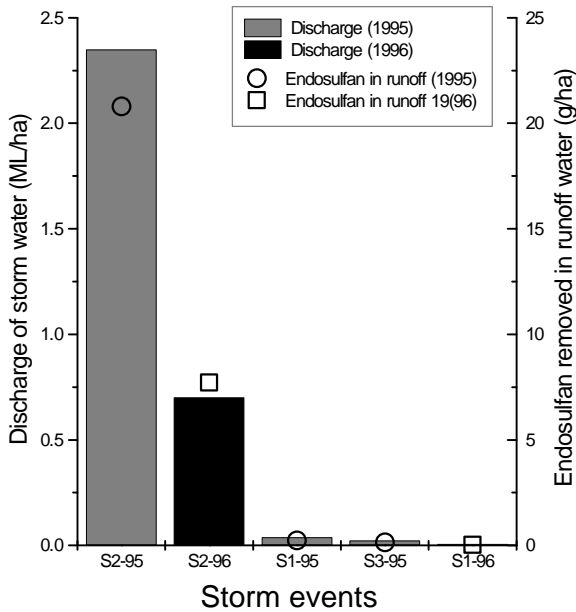
Pesticide loads in runoff at the outlets are similar in amount and distribution to those in the furrows. That is, for endosulfan most residues are found in the water phase and only a fraction (1/5) on the suspended solids carried by the runoff. Thus, the solubility of endosulfan in water is still sufficient to ensure that simply providing sediment traps will not allow removal of the residues in runoff. However, this distribution depends on the runoff sediment load and it was found that storm runoff has a greater proportion of endosulfan bound to sediments. Obviously, distribution to the non-sedimentable water phase applies even more to water soluble pesticides, as this is dependent upon the physico-chemical characteristics of a compound.



**Figure 11. The endosulfan load in runoff waters depends on the time since the field was last sprayed**

The amounts of pesticide being exported in runoff depend mostly on the time since the field was last sprayed (Fig. 11), being higher soon after spraying. In irrigation waters, these loads are only a small proportion (1 to 3%) of the pesticide present in the field soil, but the residue concentrations are still of environmental significance. By contrast, a major storm event could more effectively erode all the soil surface on cotton fields, moving up to 10% of the pesticide from the field (Kennedy *et al.*, 1997). Minor storms produce little or no discharge through the outlet (Fig. 12).

From observations in one field at Warren it was calculated that the total amount of endosulfan



**Figure 12. Minor storms produce little or no discharge through the outlet**

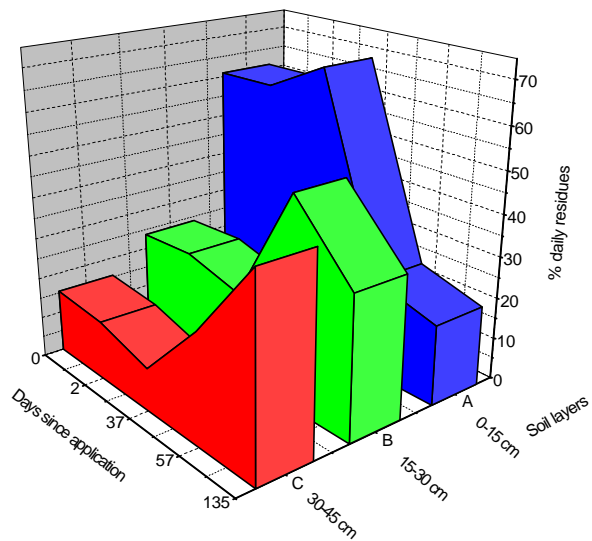
in runoff leaving the field, after six irrigations and three storms, amounted to 41.2 g/ha, that is 2% of the total endosulfan applied on that field in the three sprayings of the 1994/95 season. This percentage may seem trivial, but in fact, in terms of environmental safety, it is serious if discharged into the riverine system because fish and other aquatic organisms are susceptible to very low pesticide concentrations in water. For instance, endosulfan concentrations in runoff ranged from about 7 µg/L six days after spraying to 0.15 µg/L for the last irrigation of the season (56 days after last spraying took place), while the toxicity level to freshwater fish LC<sub>50</sub> is the range of only 0.1-2 µg/L. It seems possible, therefore, that runoff from early irrigations and storms could cause fish kills, even if runoff is diluted in the river water. For less toxic chemicals this range of concentrations would be of less concern.

**Mobility and leaching to ground water**

Movement of pesticides in the soil environment, or from the soil to other environments, is determined by both the physico-chemical properties of each specific compound, the type of soil and climatic conditions, rainfall in particular.

Leaching is pesticide movement from the soil surface into deeper layers by diffusion. Sandy soils are more prone to leaching because of their permeability and low binding capacity (see Sorption below). Clay soils will tend to capture the pesticides molecules and restrain their mobility. Water soluble pesticides are the more hazardous to the environment since they can be leached after rainfall and irrigation events, moving eventually into water systems. Once a pesticide has leached through the soil it may contaminate ground water, and if this water is used (bore water) it could be brought back to the surface and spread the contamination elsewhere.

Apart from the soil conductivity, the extent of leaching is determined by the solubility, sorption properties and rate of degradation of a particular pesticide. Generally, cotton soils in Australia have low hydraulic conductivity and leaching of pesticides to ground water is not a great concern at present, though it happens (Fig. 13). However, there is potential for leaching for very soluble pesticides such as most herbicides, the fungicide metalaxyl, the defoliant dimethipin, ethephon and endothal and some insecticides - methomyl, aldicarb and dimethoate in particular. In the past, atrazine posed a serious concern in the cotton in-

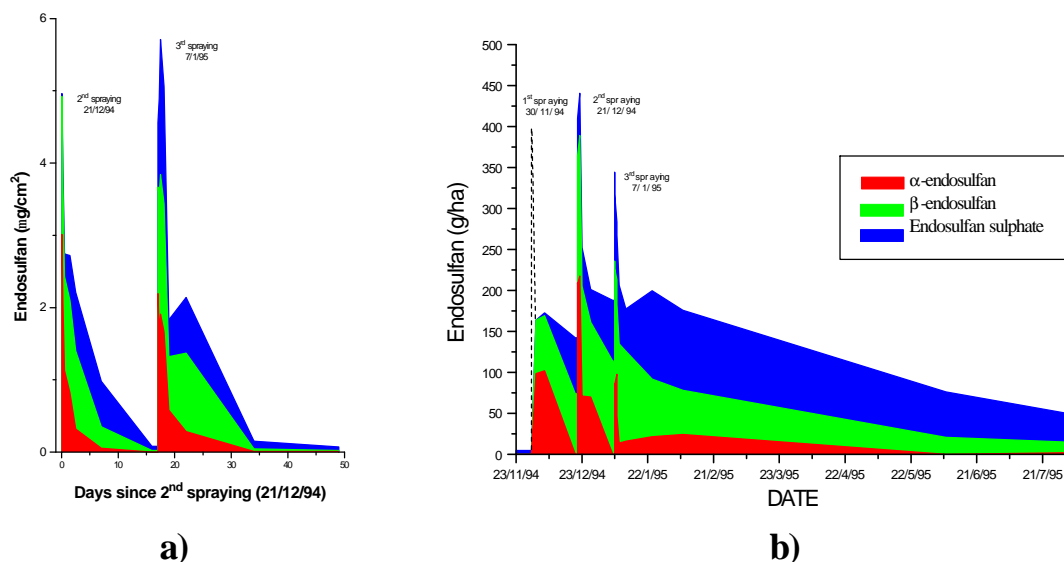


**Figure 13. Movement of a herbicide down the profile in a vertosol of the Namoi valley**

dustry because of its persistence and leaching, but it is not registered for use now. Currently, a number of herbicides appear regularly in rivers of cotton growing areas (Muschal, 2000), and this contamination is most likely due to leaching rather than surface runoff. In contrast, most insecticides are unlikely to leach because of their high affinity for soil organic matter. For instance, endosulfan does not move deeper than the first 10 cm of soil with most residues found above 5 cm depth in undisturbed soil (Kimber *et al.*, 1995). Practically all the endosulfan found in water comes from drift and volatilisation or surface runoff after large storms. Similarly, pyrethroids are very unlikely to leach because of their extremely low solubility in water and high adsorption onto soil organic matter.

### Degradation of pesticides in cotton production systems

Although pesticides may be transported away from the site of application, their main dissipation is by natural degradative processes. This degradation takes place *in situ* by chemical, biological or photodegradative processes. As an example, the time course after spraying for dissipation of endosulfan in cotton fields is shown in Figure 14. These profiles indicate transport processes such as volatilisation and runoff in surface water as well as degradation *in situ*. Most of the dissipation observed in the first few days is by the physical process of volatilisation rather than degradation. The patterns for foliage and soil are similar, although soil can be seen to stabilise beta-endosulfan and the sulphate product which persist on field much longer. Unlike predecessors such as DDT, endosulfan dissipates rapidly, with the formation of endosulfan sulphate as a major degradation product. Unfortunately, endosulfan sulphate is also toxic to fish and aquatic biota (Sunderam *et al.*, 1992), and residue analysis should take into account all three forms.



**Figure 14. Dissipation of endosulfan: a) in foliage; b) in soil (Warren, field 4 1994/95)**

For each chemical, various degradation paths are found according to the nature of the substrate (soil, water, or plant tissue), while the rate at which degradation takes place depends on both its chemical properties and a number of environmental factors such as pH, temperature, sunlight wavelength, moisture, etc. With a few exceptions, i.e. aldicarb, degradation products are often less toxic than the parent compounds. Desirable degradation products are carbon dioxide, water, mineral

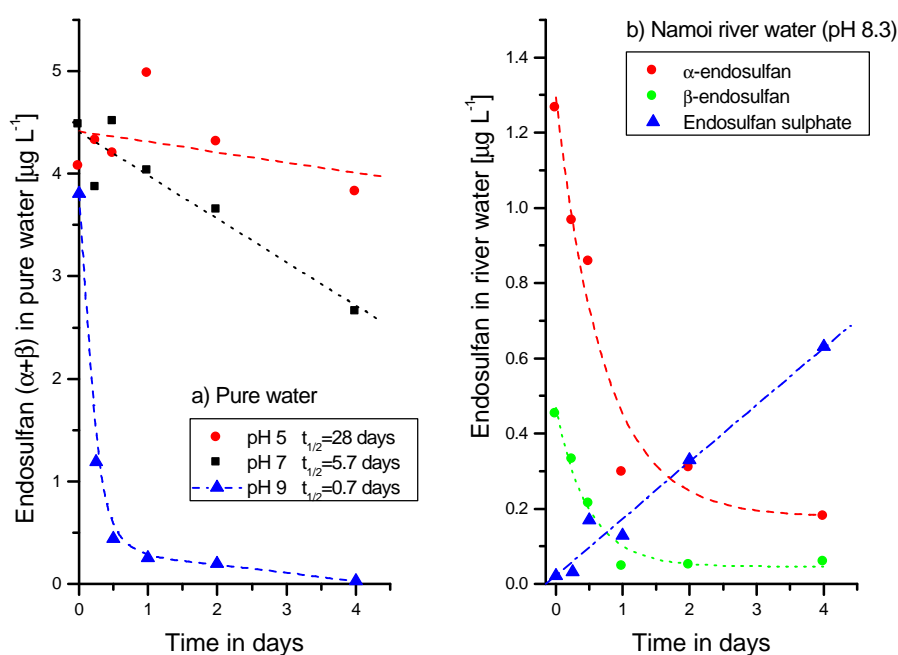
salts and other harmless metabolites naturally occurring in soil and humic substances. Following is a description of these degradative processes, a summary of which for specific cotton pesticides is given in Appendix 2.

### Chemical degradation

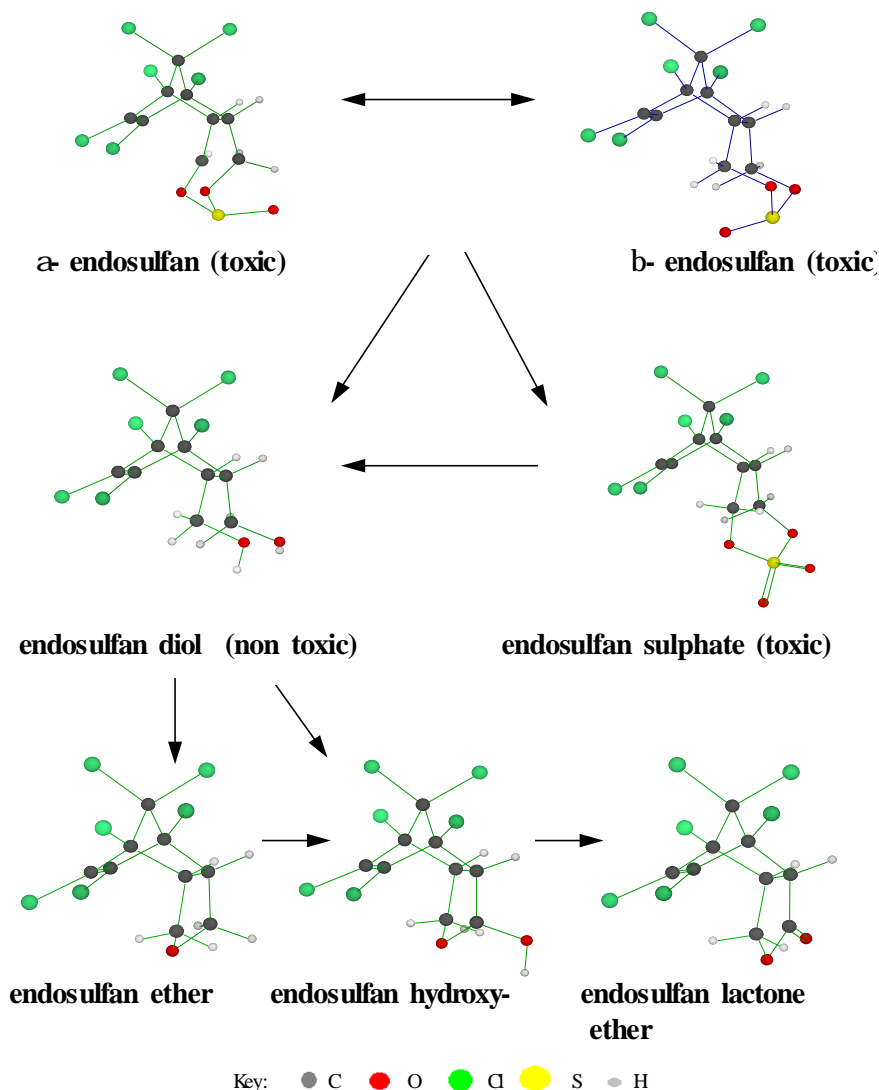
Most chemicals used in agriculture, particularly pesticides, are stable under a narrow range of physical conditions. Because of the changing nature of the environment, these chemicals can be decomposed whenever there is a change in the factors controlling their stability.

The most common chemical processes in the field are hydrolysis by reaction with water and oxidation by air, while isomerisation, reduction, and binding to other chemicals play a complementary role. In normal field conditions, all these processes act together. Important climatic factors affecting degradation rates are temperature and moisture. Higher temperature increases the rate of chemical reactions, while water facilitates the reactivity of the molecules involved. In addition, chemical reactions may be catalysed in several ways. Catalysts include clay surfaces, metal oxides, metal ions, organic surfaces and other materials found in soil (i.e. extracellular enzymes), all of them helping speed up the degradation process.

Hydrolysis is the main degradation pathway for pesticides in nature, occurring in free waters as well as moist surfaces, soil and groundwater. Most microorganisms, animals and plants also used hydrolytic reactions to metabolise pesticides. An important factor controlling hydrolysis is the pH of the media. Increasing pH generally increases the rate of chemical degradation of organophosphates, endosulfan (Fig. 15a) and other insecticides, but for some pesticides acidic conditions (pH < 7) may foster hydrolysis, as in the case of atrazine. The pH of river waters usually varies between 6 and 8, whereas soils used for growing cotton in Australia are usually alkaline, with vertosols usually being in the range 7.5 - 8.5 which provide good conditions for chemical degradation of most pesticides.



**Figure 15. Degradation of endosulfan in water under acidic, neutral or alkaline conditions (a), and formation of the sulphate product in river water (b)**



**Figure 16. Endosulfan and its five degradation products. Pathways after Miles and Moy (1979)**

Oxidative reactions are particularly important in the breakdown of pesticides. As a result of oxidation many chemicals that were originally hydrophobic become more water soluble and can move into aqueous phases to undergo further breakdown by hydrolysis and microbes. Such is the case of many organophosphates and pyrethroids. Oxidation can also be mediated by soil and water microorganisms. Compounds in a highly oxidised state, such as the chlorinated hydrocarbon insecticides, may tend to resist further oxidation under aerobic conditions, but may be susceptible to reductive attack under anaerobic conditions in sediments or deep soil layers. Alternatively, compounds in a highly reduced state are more susceptible to decomposition under oxidative conditions than under reducing ones. Trifluralin is a good example of this.

Hydrolysis of endosulfan forms endosulfan diol, a non-toxic form found normally in water (Peterson and Batley, 1993), where it can undergo further alteration by alkaline hydrolysis to produce endosulfan lactone, also a non-toxic compound (Fig. 16). Oxidation of endosulfan yields the sulphate form, a product of less toxicity than the parent isomers (Williams and Chow, 1993), but about 10 times more persistent in soil than alpha- and beta-endosulfan (Kimber *et al.*, 1995).

Additional conjugation reactions often further increase the water solubility of the pesticide following reaction with sugars, aminoacids or other water soluble molecules found in soil or water. This is a process mainly found in biological degradative systems within cells, or by extracellular enzymes found in soil.

Isomerization of certain pesticides may turn the original active compounds into less toxic forms. This process may be triggered by a change in pH, by light or other environmental factors. For instance, lambda-cyhalothrin undergoes isomerization in soils and water, the rate being much faster in alkaline water (pH 9) than in neutral water (Wang and Kennedy, 1995).

Finally, pH and organic matter content are the main factors affecting chemical degradation in soil, while clay, iron, copper, and aluminium oxides act as catalysts in many degradative reactions. In general, a high pH in soil will decrease the sorption of anionic pesticides making them more available for chemical and biological degradation. The opposite effect occurs with increasing organic matter, which usually tends to capture pesticides, although sometimes organic matter may counter-balance this negative effect by providing substrates for microbial breakdown.

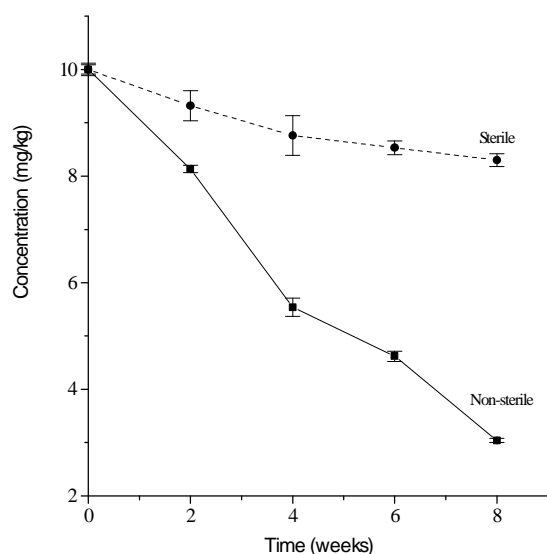
### ***Photodegradation***

Sunlight, particularly in the ultraviolet (UV) range below 350 nm provides sufficient energy to affect photochemical transformations in organic molecules such as pesticides. Photodegradation may take place in water, in air or on exposed surfaces of soil, plants or biofilms. The photochemical behaviour of a pesticide in each of these media is influenced by a different set of environmental variables, possibly leading to several chemical pathways for photo-decomposition.

In the atmosphere, photooxidation is thought to occur as a result of plentiful oxidant, sunlight, and catalytic surfaces (dust, droplets) or other reacting substances ( $\text{NO}_x$ , hydrocarbons,  $\text{O}_3$ ). Volatile compounds sensitive to light that have evaporated to the atmosphere would be degraded in this way. In the case of endosulfan, a half-life for endosulfan in the atmosphere of about two days at the latitude of Narrabri has been estimated (Hoechst, pers. comm.).

In aquatic environments, the pH of the solution, the quantity of oxygen available and the presence of any natural compounds that can accelerate the photochemical reactions are potent controlling variables. The pH can influence not only the rate of the reaction but also the nature of the breakdown products. For instance, the herbicide trifluralin undergoes a fast photodegradation in acid conditions, but its breakdown rate at pH 11 is only 10% of that at pH 5.5 and the metabolites produced are different (Tomlin, 1997). Similarly, the photolysis rate of trifluralin is ten times faster in aerobic conditions compared to anaerobic. Endosulfan can be degraded also by photolytic hydrolysis to produce the non-toxic endosulfan diol and this process is pH dependent (Archer *et al.*, 1972).

On soil surfaces, an array of factors can influence the photochemical reactions (Singh *et al.*, 1991). The presence of certain metal ions, organic matter, ionic forces between molecules in the matrix, moisture and pH all have an influence. For instance, parathion is not photodegraded in the atmosphere, but when sprayed onto fine road dust and exposed to sunlight undergoes a rapid photolysis. However, unlike the water medium, photodegradation in soil has little practical significance because radiant energy is absorbed by the soil itself. Thus, field trials at Warren have shown that photodegradation of endosulfan in soil and on foliage is probably insignificant (Southan and Kennedy, 1996). Another type of surface is that of oil films on water bodies, which probably dissolve the



**Figure 17. Biodegradation of lambda-cyhalothrin in soil under laboratory conditions**

pesticides from the water or those bound to particles suspended in the air that contact the surface. Similar factors as those found in water should influence the photodegradative reactions on this medium although the oil may stabilise some pesticides.

### **Biological degradation**

Living systems play a very important role in pesticide degradation. Modern agricultural chemicals are subject to degradation by plants, microbes and microfauna found in soil or water. In addition, most pesticides are metabolised by animals after being ingested. Usually, a very small number of metabolites are produced, and in the case of animals these are mostly excreted in the urine and faeces. Similar chemical processes as described above, but catalysed by enzymes, are used by microorganisms, plants and animals to breakdown pesticides. For instance, a class of enzymes known as mono-oxygenases act as effective oxidising agents.

### *Phytodegradation*

Biodegradation of insecticides in plant tissues is common, and even herbicides can be degraded by non-susceptible plants (see Appendix 2). The formation of endosulfan sulphate in soil and plants is thought to be mainly caused by microbial or plant tissue. Endosulfan undergoes conversion to the sulphate in foliage at about the same rate as in soil, but the sulphate disappears almost completely within two weeks (Fig. 14a) whereas in soil it is more stable (see Fig. 14b). This indicates the existence of a further degradative path for the endosulfan sulphate in plant tissues which is lacking in soil.

### *Microbial degradation*

The soil microbial population has one of the most profound but variable influences on decomposition of pesticides. The nature and type of population is highly influenced not only by the above climatic and soil factors but also by others like mineral content, oxygen status, organic molecules, soil structure and porosity. Microbial populations in soil will be constantly changing as substrate profiles change and this in turn leads to unpredictable rates of pesticide degradation. Certain types seem to predominate, specifically species of *Arthrobacter*, *Aspergillus*, *Bacillus*, *Corynebacterium*, *Flavobacterium*, *Fusarium*, *Nocardia*, *Penicillium*, *Pseudomonas*, and *Trichoderma*, at least in terms of those that can be isolated on laboratory media. New methods of analysis for the potential soil populations of microbes using PCR amplification of soil DNA content indicate rather different species profiles (Stackebrandt and Goebel, 1994).

Microbial degradation can be demonstrated by comparing rates of degradation of a pesticide in sterilised soil or water with that in non-sterile soil or surface water. Thus, rates of degradation of lambda-cyhalothrin in soil differed significantly between both treatments (Fig. 17), indicating that losses due to microbial activity are much more important than those by chemical degradation alone. Soil microflora also convert endosulfan to the non-toxic diol form (Miles and Moy, 1979; Guerin, 1993), whereas micro-organisms found in river waters convert it to the toxic sulphate form, a pro-

cess not observed in pure water alone (see Fig. 15b). This implies that residues of endosulfan sulphate found in the riverine environment may have been formed there after aerial transport of the parent compound and do not necessarily come from runoff discharge.

An important factor in microbial degradation of pesticides is bioavailability. Materials that are very insoluble in water or highly sorbed to the colloids of the soil avoid biodegradation even though their inherent resistance to degradation may not be that great. Chemicals initially soluble only in the organic fraction of the soil can be incorporated into more aqueous phases or the biological degradative chain after being oxidised. In this context, the product of the mono-oxygenases may foster subsequent biochemical processes. In the case of endosulfan, the formation of endosulfan sulphate is probably catalysed by mono-oxygenase enzymes.

Some soil microbes use the pesticide itself as a carbon substrate for energy, but others degrade the pesticide as a co-metabolite using other carbon compounds as the main source of energy. The latter process of co-metabolism normally occurs when enzymes in the micro-organism are not highly specific for the substrate they decompose. Thus, any pesticide having structural similarity to this substrate can be decomposed without necessarily providing significant amounts of energy to the micro-organism.

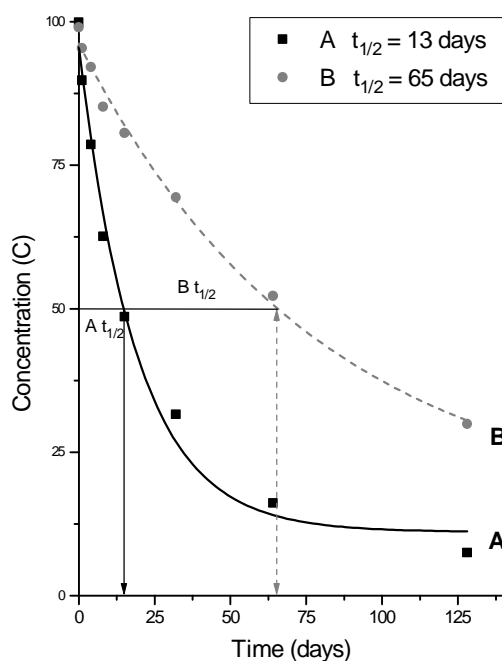
Although the rates of biodegradation by soil microbes are variable, in general it can be assumed that fertile, moist soil with a rapid turnover of organic matter will be the most active in biodegradation. It has also been observed that repeated exposure of a soil microbial population to a new chemical, over time, can lead to enhanced degradation of the chemical as a process of adaptation takes place (Harris *et al.*, 1988).

## Persistence

Although modern pesticides usually disappear quickly from the field, by one or other of the various paths of dissipation and degradation explained above, there are some exceptions. Once again, the physico-chemical characteristics of a particular chemical will determine its persistence in soil and water. Sorption to organic matter or clay, hydrolysis and bioavailability for microbial degradation are crucial features that would determine the persistence of a chemical in the environment.

### *Half-life of a chemical*

Persistence and dissipation are commonly indicated by the field half-life, which is the time necessary for half the amount of chemical applied to disappear from a site. This field half-life is the result of a combination of several processes acting simultaneously, and as a consequence it can be hard to estimate with accuracy. The same

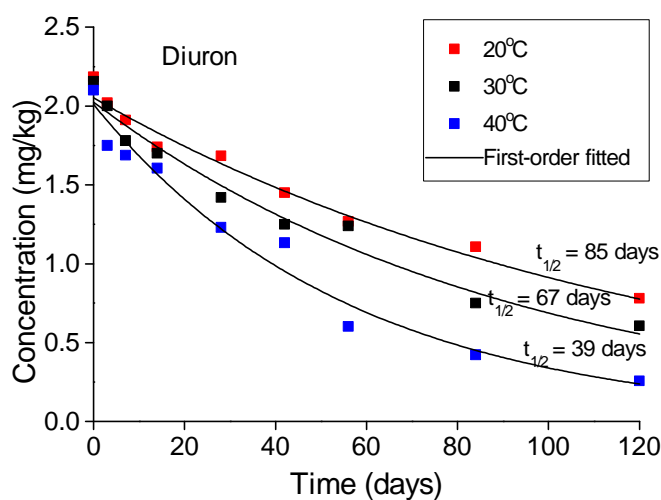


**Figure 18. Determination of half-lives**



chemical applied on different soils or under different weather conditions, for instance, may have different half-lives. For this reason, half-life figures are normally referred to particular environments, or given as a range and they should be used as an indicative guide only.

The field half-life of a particular chemical is strongly determined by its physico-chemical properties and varies according to the medium: air, water, soil and organic matter. From time course data it is possible to calculate half-lives (Fig. 18) in most of these media according to the following mathematical model:



**Figure 19. Half-life of diuron in soil at three different temperatures**

$$dC/dt = -kC, \text{ where } C \text{ is concentration, } t \text{ time and } k \text{ a constant}$$

For a first-order reaction, the rate constant for this equation is  $k = \ln (C_0/C_t)/t$ , and the half-life ( $t_{1/2}$ ) is calculated as

$$t_{1/2} = -2.303 \ln(0.5)/k = 0.693/k$$

Chemicals with a calculated half-lives of only a few days dissipate quickly in field situations and leave no detectable residues. Pesticides with half-lives longer than four months are expected to remain on the field for more than a year and can build-up from one season to the next. However, various factors in the field can change the half-life of the chemical, shortening it by faster degradation or lengthening it due to a strong sorption of the chemical to organic matter in the soil and to clay. For example, the half-life of diuron can be reduced from 85 to about 40 days by doubling the soil temperature (Baskaran *et al.*, 1999; Fig. 19).

In laboratory trials conducted at The University of Sydney, the half-lives of the isomers  $\alpha$ - and  $\beta$ -endosulfan in water at pH 8.5 were calculated (Southan and Kennedy, 1995), and the results are given in Table 5. From these values, and considering its volatility, endosulfan can be expected to dissipate very rapidly from runoff waters on field. Unfortunately, in a field situation endosulfan is bound to soil, and only a small proportion that is carried in the runoff experiences hydrolysis. Further, endosulfan sulphate is much more stable than the parent endosulfan and remains in soil and water much longer. Half-lives of endosulfan and its sulphate product in soil have also been studied in Australia (Kimber *et al.*, 1995) and Canada (Stewart and Cairns, 1974). The disparity in the

values obtained (Table 5) is probably attributable to differences in temperature or other environmental factors that control degradation processes. In our field trials, half-lives of endosulfan in soil were much shorter still immediately after spraying, perhaps as a result of a rapid initial volatilisation from the soil surface. Thus, both field and laboratory

**Table 5. Half-life of endosulfan in water and in soil (days)**

	Water	Australian soil	Canadian soil
Alpha-endosulfan	4.7 ± 0.3	43	60
Beta-endosulfan	1.5 ± 0.2	76	800
Endosulfan sulphate	-	101	-

studies are necessary in order to determine what will happen in real situations. Field half-lives in soil for the most common pesticides are indicated on Appendix 3.

### Sorption to soil

The removal of a chemical species from a fluid phase (gas or liquid) by its association with a solid phase is called sorption. The term *absorption* refers to sorption into ‘pores’ of the solid, while *adsorption* is for sorption on to the surface of the solid. Sorption is usually mathematically expressed by the desorption coefficient  $K_D$ , which is calculated as the ratio of sorbed to solution pesticide in a water-soil slurry, a measure of the relative affinities of the pesticide for water and sediment. For each chemical there are as many  $K_D$  values as soil types, but a mean value or a range of values for a group of soils (sands, loams and clays) is sufficient to understand the sorption properties of a particular compound. High values of  $K_D$  are associated with a great persistence of the chemical in the soil because of poor bioavailability. For instance, the herbicides diuron and prometryn have higher  $K_D$  than fluometuron or pyriithiobac sodium (Staple®), as shown in figure 20.

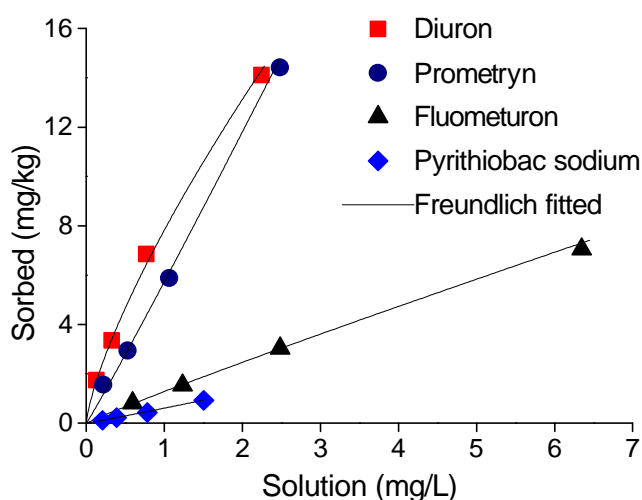


Figure 20. Sorption of four herbicides in soil/water

The partition coefficient between *n*-octanol and water ( $K_{ow}$ ) is a useful property determined in laboratory experiments, because it allows a prediction of the affinity of a substance for organic matter. In soil, the latter property is measured by the  $K_{oc}$  coefficient, which depends on the organic content present in a particular soil. Thus,  $K_{oc}$  expresses the binding onto specific soil types, whereas  $K_{ow}$  refers to affinity for organic solvents. High values of both these coefficients indicate a great tendency for the chemical to bind to organic matter and remain in soil or sediments, whereas low values indicate little persistence. Pesticides of particular concern are listed in Appendix 4.

The adsorption of pesticides to soil surfaces is of particular environmental importance, for it can reduce substantially their movement off field, by leaching, volatilisation or runoff, and at the same time facilitate the biological degradation of the pesticide on the field. However, persistent insecticides can remain bound to organic material indefinitely unless breakdown by weathering agents make the chemicals available for microbial degradation in soil or water.

Sorption to organic materials such as seeds, trash, plant litter, and soil organic matter is also important. Analyses of cotton trash and litter have revealed the presence of small amounts of endosulfan and chlorfluazuron (Helix) about nine months after the insecticides were applied to the field (Table 6). Both insecticides persist there because they are bound to organic matter. Similarly, residues of endosulfan in pasture contaminated by drift

Table 6. Residues of endosulfan and chlorfluazuron (Helix) in field and gin trash

Type of material	Endosulfan (mg/kg)	Chlorfluazuron (mg/kg)
Foliage litter	0.34	2.50
Stalk litter	0.14	1.04
Gin trash	0.23	0.87
Cotton lint	<0.01	<0.05
Cotton seeds	<0.01	<0.05

have been measured, while their dissipation in time has been studied (Kennedy *et al.*, 1998a). This fact implies that animals feeding on contaminated plants nearby cotton fields are exposed to pesticides residues for a period of time before those residues disappear.

**Table 7. Endosulfan residues (mg/kg) in pasture contaminated by drift**

	Green pasture		Dry pasture	
	10 m	100 m	10 m	100m
1 day	40.68	3.47	28.75	1.15
8 days	2.04	0.70	4.52	0.36
15 days	0.61	0.23	1.32	0.36
37 days	0.22	0.07	0.51	0.14
Half-life ( $t_{1/2}$ )	5.6 days	6.9 days	7 days	14 days

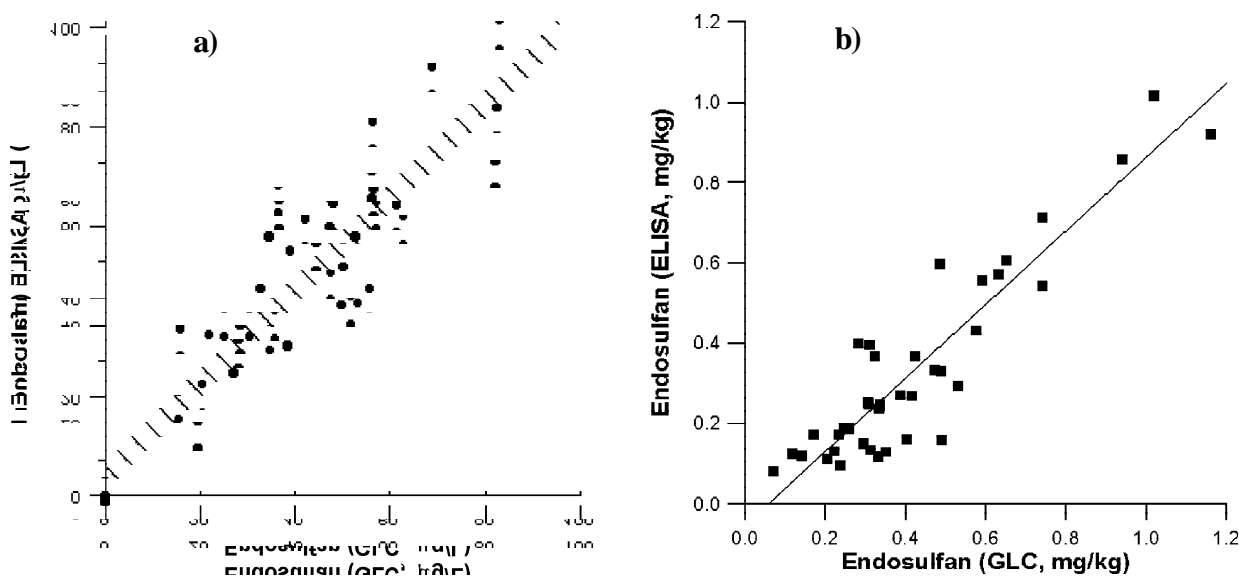
*With-holding periods*

With-holding periods for several types of feeding must be established for all pesticides to avoid livestock contamination, and this information is usually found on the label of each product. For instance, the with-holding period for endosulfan in pasture is 28 days, as it takes about four weeks for drift residue levels to reach concentrations of 0.1 mg/kg or less, which is its maximum residue level (MRL) allowed in meat. But the time could be longer for dry pasture (Table

7), since residues may remain tightly bound to the plants until weathering conditions break them down. In this sense, the established periods are only a guideline and cannot ensure any forage material is residue-free.

**Monitoring of residues - Immunoassays**

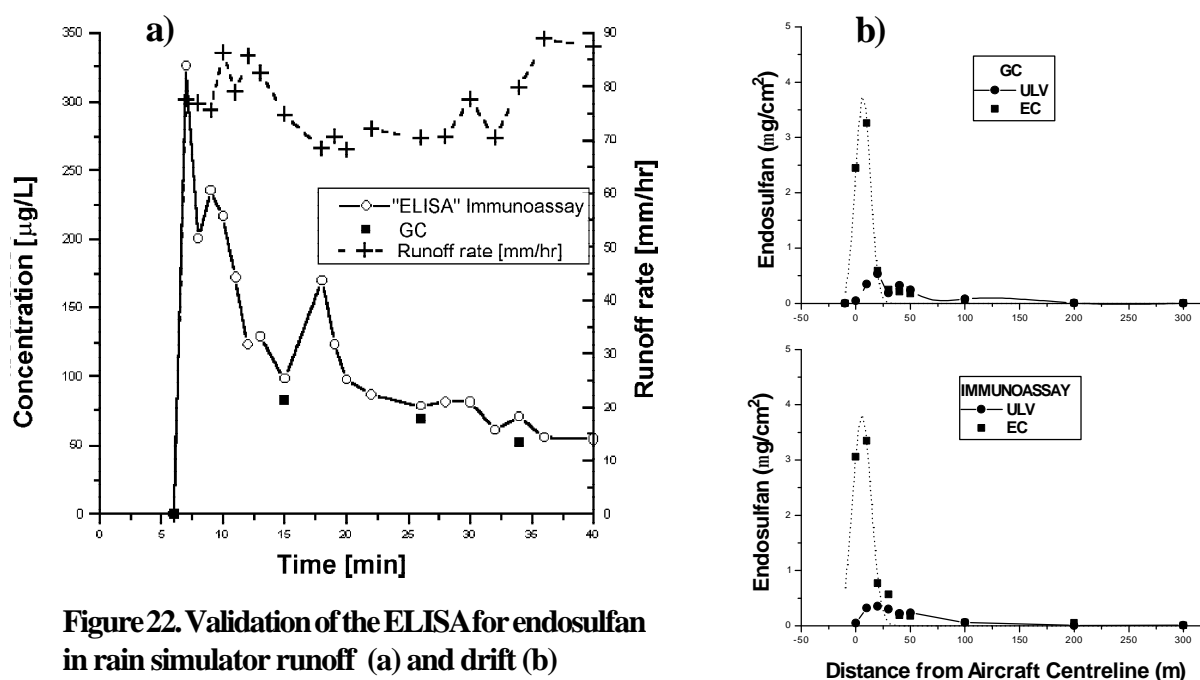
Pesticide residue analysis is expensive. Current analytical methods by both gas and liquid chromatography (GLC) require long extraction and preparation times, resulting in high costs as they are labour intensive and time consuming. For this reason, field studies on the fate and transport of pesticides and monitoring of rivers or food stuffs for residues are often unaffordable. Recently, however, new techniques using biosensors and immunoassays (ELISA) have been developed with the aim of reducing analytical costs while ensuring the integrity of the results.



**Figure 21. Validation of the immunoassay (ELISA) for endosulfan in water (a) and soil (b)**

ELISA is mainly a tool to assist in monitoring residues in grain and other produce (Skerritt *et al.*, 1998), whereas the possibilities of being applied to environmental studies have just started. Validation of the new techniques is essential before their widespread use in monitoring programs. As part of the CRC research during the 1993-96 growing seasons, a new endosulfan immunoassay produced by CSIRO was subjected to very extensive field validation (Lee *et al.*, 1997), whereby more than 1000 field soil and water samples were extracted and analysed by gas chromatography at the BCRI laboratory, NSW Agriculture at Rydalmere and at the same time by this immunoassay. This validation has shown good correlation between ELISA and GLC for both water (Fig. 21a) and soil (Fig. 21b). Indeed, this immunoassay has even contributed to improvements in the protocols for sampling and analysis by extraction using organic solvents and GLC (Kennedy *et al.*, 1998b).

The outcome is important, and allowed future research on endosulfan and other cotton pesticides to be conducted more cheaply. The endosulfan immunoassay is applicable whenever the total concentration of the toxic forms of endosulfan is an adequate result, as it does not allow the different chemical forms to be distinguished. The sensitivity of the ELISA is comparable to that of chemical assay by gas chromatography. Other collaborative studies in the LWRRDC/CRDC/MDBC program benefited from its use (Fig. 22), specifically the pesticide transport associated with erosion (Silburn *et al.*, 1995) and drift of EC and ULV formulations from aircraft (Woods *et al.*, 1998a).



**Figure 22. Validation of the ELISA for endosulfan in rain simulator runoff (a) and drift (b)**

Since this research started, new ELISAs for diuron and DDE were prepared (Beasley *et al.*, 1998) and used in surveys of DDT residues in soil (Shivaramaiah *et al.*, 1998). In preparing pyrethroid immunoassays the best assays were selected for full characterisation, with one for broad specificity and others for compound-specific assays (including deltamethrin and bifenthrin). ELISAs for the benzoylphenylurea family which were also developed for group specificity (Wang *et al.*, 1999). More work on immunoassays for organophosphate and carbamate insecticides is currently under way, funded by the GRDC. Validation of the ELISA for pyriithiobac-sodium (Staple) using soil from cotton fields in the Namoi valley was done in preparation for a full study on the fate of this new herbicide under field conditions (Mitchell *et al.*, 1999). Finally, ELISA has also been used successfully to monitor pesticide residues in wildlife (Sánchez-Bayo *et al.*, 1999a).

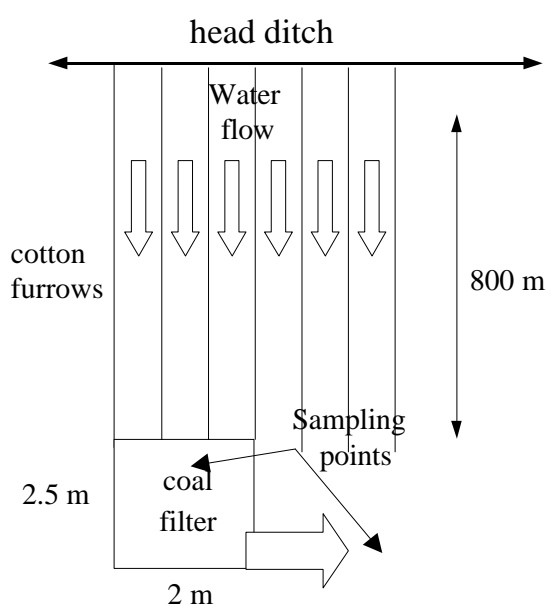
## Containment of chemicals

In the previous section, a discussion on the dissipation and degradation of pesticide contaminants found in cotton farms has been presented and illustrated with experimental data. The aim of the second CRC project was to develop buffering techniques to maximise the retention and breakdown of nutrients and pesticides on cotton farms, and it was approached in the three stages discussed below.

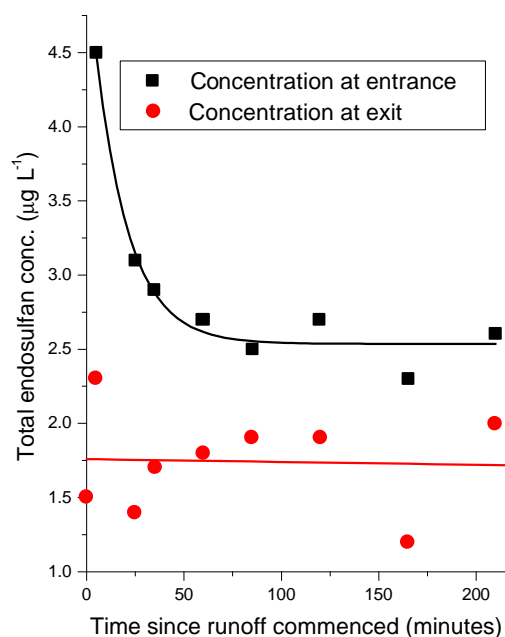
### Adsorptive remediation of runoff from cotton farms

In this phase of the project, commenced in 1994, a range of potential adsorbents were examined to determine their adsorption – desorption characteristics with respect to pesticides used for cotton growing. These characteristics were determined using classical batch adsorption techniques in the laboratory. Endosulfan and chlorfluazuron were chosen as chemicals suitable for remediation studies, however the latter chemical was abandoned after its withdrawal from the cotton industry. From a number of bulk media examined as potential adsorbents, coal was selected as having features suitable for large scale adsorptive remediation. Laboratory work showed that coal was effective in adsorbing all three endosulfan isomers with binding for  $\alpha$  and  $\beta$  being stronger than that for endosulfan sulphate (Hugo, 1999).

A field trial was initiated whereby coal was positioned at the exit of three furrows of an irrigated cotton field at Cumberdeen, Wee Waa (Fig. 23). The coal had an average diameter of 20 mm and covered an area of approx 5 square metres to a depth of 15 cms. A standard irrigation of the field was then carried out. Water samples were taken from the furrow exit/coal bed entrance and from the coal bed exit. Results are shown in figure 24, and indicate a substantial reduction in endosulfan content between entry and exit points.



**Figure 23. Schematic diagram of coal filter placement in field trial**



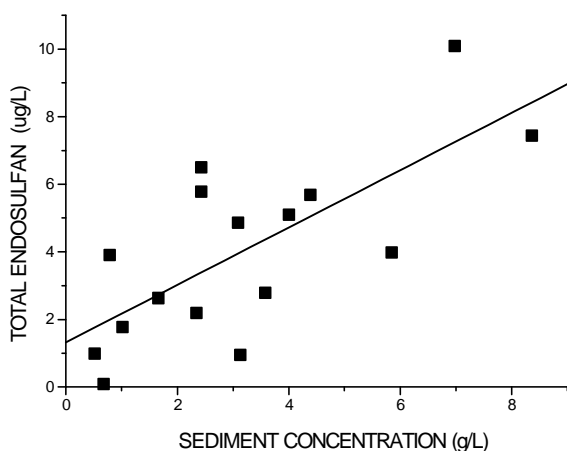
**Figure 24. Total endosulfan concentration at entry and exit of coal filter**

### Sediment traps and flocculation to prevent transport of pesticides in runoff

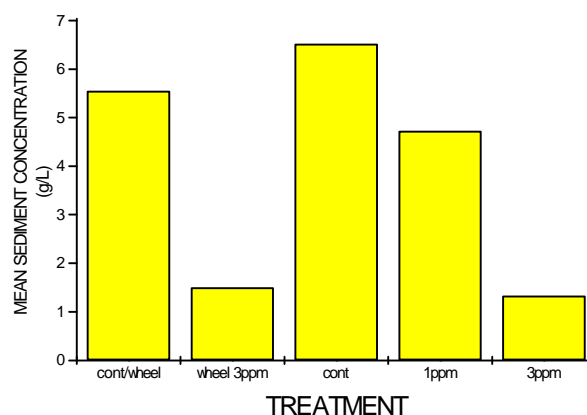
This phase of the work consisted of a trial on the use of polyacrylamide (PAM) as a flocculant on cotton fields to prevent sediment transport. Sediment traps, based on well known hydrological principles, result in deposition of suspended sediments; however, no research specifically on such traps has been performed on Australian cotton farms before.

Irrigated cotton requires careful slope control to avoid soil erosion, though some is inevitable. As a result, runoff from such irrigations often contains significant loadings of eroded sediment. Most insecticides have strong soil binding properties and are associated with this sediment fraction (Fig. 25), although considerable amounts in non-sedimentable fractions has been noted in field runoff containing endosulfan (see above).

It was proposed that the control of the sediment in run-off during irrigation could possibly reduce the transport of endosulfan off-field. Various erosion control measures, both physical (e.g. stubble retention) and chemical (e.g., flocculants), may be employed to control this sediment run-off. In our study, an anionic polyacrylamide (PAM) synthetic flocculant commonly used in water treatment was applied to the head ditch irrigation channel prior to the water moving onto the field. The effect of traffic compaction on erosion was also studied, with compacted furrows exhibiting lower erosion than the non-compacted furrows. The trial was conducted later in the cotton season, a month after the application of endosulfan had ceased and when the degradation product, endosulfan sulphate, was the major chemical species present in the runoff.



**Figure 25. Concentration of endosulfan residues and total sediment load in runoff**



**Figure 26. Sediment concentration in runoff water treated with PAM**

The objective was to determine the effect of sediment loads on pesticide transport from field furrows. For this trial, Allied Colloids provided materials, equipment and personnel. The field was freshly cultivated and the soil was highly erodible. Erosion and pesticide movement under three levels of polymer application (0, 1 and 3 mg/L PAM) was measured. It was obvious, from direct observation of the relative clarity of field runoff samples treated with PAM, that dramatic differences in pesticide bound to sediments could be expected. Mean sediment concentrations in runoff of 6.5, 4.8 and 1.3 g/L were recorded for 0, 1 and 3 mg/L treatments respectively (Fig. 26), indicating a strong effect of the polymer in reducing the sediment load.

Although it is difficult to see how polymers such as PAM can readily be applied to control erosion during storms, the data available indicates they have a very significant effect during irrigations (Hugo *et al.*, 1996). It is relatively easy to apply PAM to irrigation water, but its cost-effectiveness in reducing erosion of sediments and in containing pesticide residues still needs to be assessed. It is also possible that PAM could affect the degree of solubilisation of endosulfan, for example, by flocculating humic materials in water. This would be a bonus enabling sediment traps to function more effectively, but its ability to control residue transport depends entirely on whether the pesticide is adsorbed to erodible sediments.

### **Containment in gravel/soil filters using biofilms**

This approach to pesticide residue retention involved directing runoff into filtration beds supplied with microbial biofilms. The technique has been tested in the laboratory using atrazine-degrading microbes isolated after perfusion of a grey-cracking clay for three years with a dilute solution of atrazine (Van Zwieten and Kennedy, 1995).

In principle, this approach, which involves containment plus bioremediation as discussed in the next section, can be extended to other pesticides and herbicides. Preliminary trials, in which atrazine was completely degraded, could be extended to similar triazine pesticides used in cotton growing i.e. prometryn, provided engineering problems associated with field treatment of surface water or sediments could adequately be addressed.

## **Bioremediation**

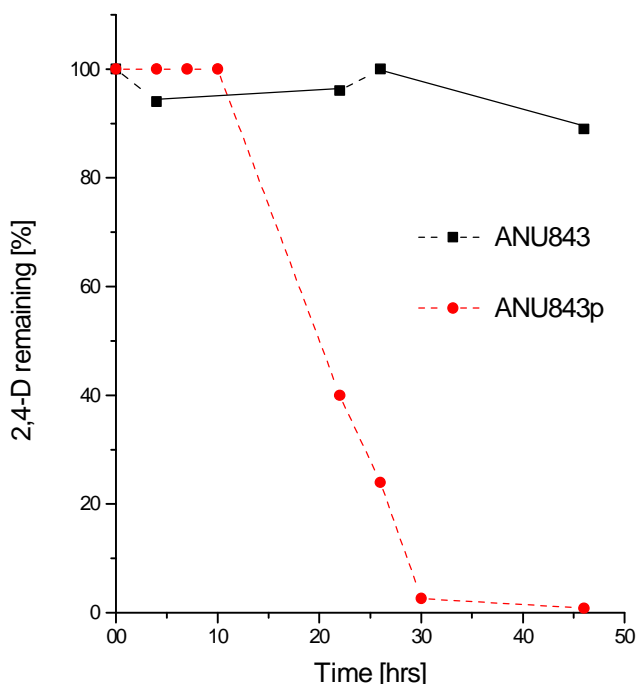
Degradation processes are an important component of the natural dissipation of pesticides in the environment, with most degradation due to biological intervention which can be considered as bioremediation. Environmental factors such radiation, temperature, moisture content of soils and the presence of other substrates control the rate of this natural remediation, as discussed earlier. However, bioremediation of pesticide residues can be enhanced by modifying these conditions - for instance, it can be expected that cultivation may increase the rate of remediation by mobilising nutrients and favouring degradation of residues by aerobic microorganisms.

Using bioremediation as a tool for eliminating pesticide residues is thought to be an effective, clean and probably cheap way of reducing the environmental impacts that result from application of pesticides in cotton production. The first CRC project on *in situ* bioremediation of soils commenced in early 1994, but was abandoned when a post-graduate scholar resigned from the program a year later. Currently, a second attempt to apply this concept on cleaning contaminated tailwaters is under way.

### ***In situ* bioremediation of soils**

Initial work was directed towards *in situ* bioremediation of a few pesticides, namely endosulfan, because of its high usage and high profile; lambda-cyhalothrin, as a representative of the pyrethroids; and chlorfluazuron, as a newcomer with considerable potential use.

Development of systems for the isolation of pesticide-degrading microbes was the first priority. Because the pesticides chosen had poor solubility in aqueous systems, a variety of methods for incorporating the chemicals into microbiological media and soil test systems were tried. The main objective was to devise systems which would allow quantitative analyses of the chemicals so that



**Figure 27. Biodegradation of the herbicide 2,4-D by transconjugant strains of *Rhizobium trifolii* ANU843p**

from the effect of this herbicide at concentrations 5-10 ppm in the nutrient solution (Kennedy *et al.*, 1995). This proves that *Rhizobium* strains are effective at degrading 2,4-D, whether acting in nodules or in the rhizosphere (Fig. 27). Similar work was performed using transconjugants of *Azospirillum brasilense* associated to the roots of cotton plants, which provided similar protection (Feng and Kennedy, 1997). The azospirilla on cotton plants were also capable of nitrogen fixation in the laboratory, providing a possible bonus to their bioremediating capacity.

The advantages of associating microorganisms such as *Azospirillum* capable of pesticide degradation are two-fold. Firstly, the accelerated biodegradation of the pesticide can bioremediate the soil. In addition, a 'bio-safening' effect on the plant can be gained, so that cotton plants can be protected against the herbicidal effect of residual 2,4-D in soil from applications to other crops in rotation (e.g. wheat).

(ii) a consortium of soil microorganisms capable of degrading the triazines, atrazine and prometryn, has been prepared as a soil inoculant. These cultures are being further investigated for their potential to provide protection and bioremediation of these herbicides (Van Zwieten *et al.*, 1994).

(iii) laboratory work with a cyanobacterium (*Anabaena sp.*) has shown that this microorganism is capable of degrading lindane (Shivaramaiah and Kennedy, 1996). This system will be examined for its ability to degrade DDT residues (DDE) and other organochlorines such as endosulfan, of more significance in Australian cotton production systems. Preliminary results indicate a rapid and complete disappearance of endosulfan or endosulfan sulphate residues.

The research on bioremediation is innovative, and the results so far obtained in this CRC project are only the beginning of what promises to be crucial research in the future of agricultural systems.

the kinetics of degradation could be investigated. Pesticide-coated sand was used to incorporate the chemicals into the different test systems and some accelerated degradation was noted with certain laboratory-cultured bacterial strains.

More intensive efforts were made to isolate not only individual microbes capable of degrading particular chemicals, but also microbial consortia and/or co-metabolic microbes. Work on endosulfan residues was anticipated to concentrate on the fate of endosulfan sulphate. Herbicides to be studied were fluometuron and diuron, for which an immunoassay is available. Work on plant-microbial associations made some progress in the following areas:

(i) transconjugants of *Rhizobium* capable of nodulating *Dolichos lablab* were found to degrade 2,4-D (Feng *et al.*, 1994), thus providing protection to *Dolichos* plants



## Risk Assessment

The above research is only the necessary step towards a better understanding of the dynamics of pesticides in agro-ecosystems. This knowledge is essential for an assessment of the risk derived from the application of such chemicals.

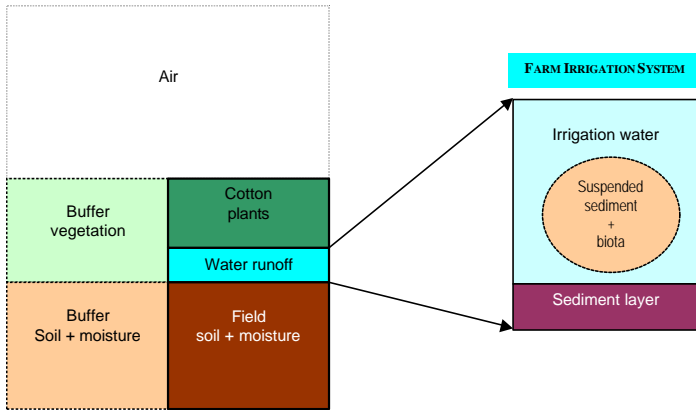
At this point, it must be realised that a balance between the profits made in cotton production and the costs associated with the methods used (i.e. pesticides) must be sought if the industry pursues both economic viability and ecological sustainability. As in any other agricultural enterprise, cotton depends entirely on the natural capacity of the ecosystems that provide productivity, and it follows that severe impacts on the environment may impair the ability of such ecosystems to provide the desired levels of production. On the other hand, off-target effects of pesticides cannot be avoided, and these must be evaluated as part of the environmental cost implicit in agricultural enterprises, while the ancient principle "means do not justify the end" should always be borne in mind. The purpose of a risk assessment is precisely to evaluate the hazards posed by pesticides used in existing cotton farms or in new cotton developments.

### Impacts on the environment

Excessive use of pesticides harms the cotton industry in several ways. Firstly, large quantities of insecticides leads to faster insect resistance, making ineffective the integrated management strategies already in place; similarly, weed resistance render herbicides inefficient. Secondly, overuse squeezes the profit margins and makes it is undesirable from the economic point of view. Finally, pesticide residues in the nearby environment may cause health problems, livestock contamination, depletion of fish and other unknown effects on wildlife and the ecosystems at large. From the environmental perspective, too much chemical applied increases the risk of contamination and pollution of air, water, soil and produce. Apart from the possible damage to wildlife and human health, pesticide overuse could result in further regulatory restraints.

An environmental audit of the cotton industry highlighted public concern that pesticide use is threatening the health of people living within cotton growing areas (Gibb and Arbour, 1991). However, it was found that those fears were exaggerated since there was no proof that certain community health problems could be linked with pesticide usage. The persistence of chemical residues in the environment is the major problem. In this regard, the State Pollution Control Commission launched a study in the 1970s to investigate the extent of cotton pesticides residues in the Namoi Valley in response to pressure from graziers. A report was published in 1980, demanding a greater regulation of pesticides and recommending the control of DDT - it did not take long to completely ban DDT from use Australia wide in 1981. More recent examples of pesticide residues creating another class of problems, that of contamination of produce with acute economic effects on exports, can be found in the recent problems with beef from Helix and endosulfan contamination. A traceback investigation on the latter revealed that much of the meat contamination can be credited to the large quantities of endosulfan applied and drifted to nearby paddocks (Kennedy *et al.*, 1999).

Stormwater runoff poses a danger to the riverine ecosystems due to lack of control and the significant quantities of chemicals carried in the first flush (Barret *et al.*, 1991). Concern over fish kills in the late 1980s, whatever their causes, led to calls for greater monitoring of pesticide levels in NSW inland rivers. This has been a routine task of the Department of Water Resources (Land and Water Conservation) since 1991, which aims at collecting data on pesticides and other chemical residues in water so that it can be used to establish priorities for management action. The efforts to reduce the



**Figure 28. Environmental compartments in an irrigated cotton farm**

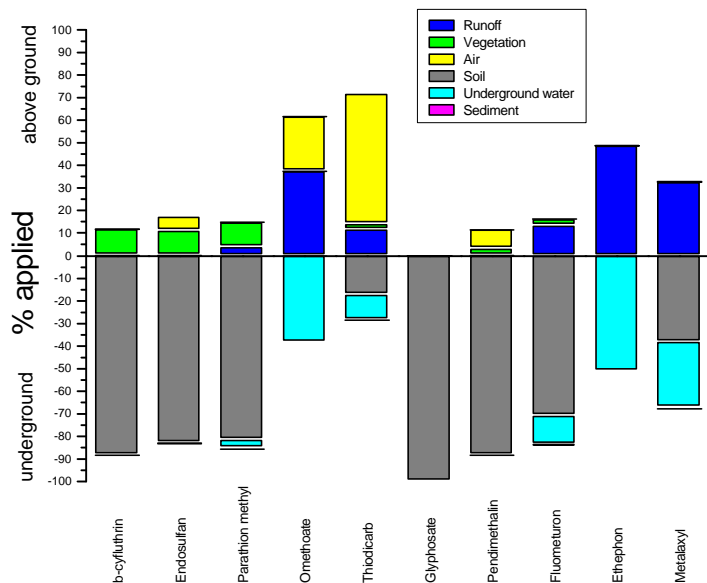
environmental impacts caused by the cotton industry have found expression in several initiatives by the Cotton Research and Development Corporation (CRDC), along with the Land and Water Resources Research and Development Corporation (LWRRDC) and the Murray Darling Basin Committee (MDBC), such as the program to minimise the impacts of pesticides on the riverine environment launched in 1993. This program used the cotton industry as a model, and as a result a best practice management manual (BPM) for all cotton growers was published in 1997.

### Modelling the distribution of chemicals using fugacity

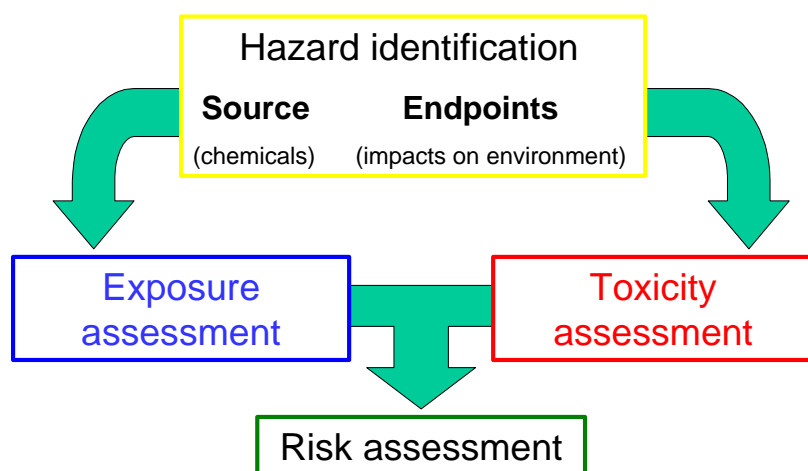
Assessment of risks cannot be done unless reliable data can be produced, and this alone warrants the research discussed in this paper. However, demand for new pesticides exceeds the resources required to study their behaviour in field conditions, as pesticide monitoring and analyses conducive to reliable data sets are time consuming and expensive. For new products, therefore, there is no alternative but modelling their fate in the environment if a risk assessment is needed.

The fugacity model (Mackay, 1991), based on a few sound physico-chemical properties of a compound, is an appropriate tool that enables to predict the distribution of pesticides in several environmental compartments found in a cotton farm (Fig. 28). In combination with drift and runoff models, it can be used to determine the concentrations of pesticide residues on field, in the buffer zones, in the tailwaters and the irrigation farm quite accurately, but it cannot predict the losses by leaching. Transport of pesticides down the soil profile has been the subject of many and complicated models, but simpler ways of estimating the likelihood of leaching have also been proposed (Gustafson, 1989). Both fugacity and leaching models can be used as complementary tools in risk assessment (Sánchez-Bayo *et al.*, 1999b).

Figure 29 shows the predicted distribution of some of the most common types of pesticides applied on a typical Australian cotton farm of 300 ha. The proportion of residues in each environmental compartment may vary from farm to farm according to the input volume of water (irrigation and rainfall), soil organic matter and vegetative cover present, though similar figures to this example can be expected. The residue concentrations, however, will vary from case to case since they are deter-



**Figure 29. Predicted distribution of residues for common pesticides used in Australian cotton farms**



**Figure 30. Framework for ecological risk assessment**

mined by the total mass of chemical applied - i.e. the rate and number of pesticide applications - and the areas affected.

### Framework for ecological risk assessment (ERA)

Risk assessments are usually based on the framework of hazard identification, exposure and toxicity (Fig. 30). Hazards are undesired events, and in an environmental context any chemical released into an ecosystem introduces a hazard, the extent of which depends on the nature

of the chemical. Risk, on the other hand, is the probability of realization of a hazard (Sutter, 1993). The first step in a risk assessment is, therefore, to identify the hazards (i.e. pesticides) and characterise the impacts they may have in a particular environment. The impacts sought vary from one assessment to another, depending on whether they affect human beings or other non-target organisms. In ecological risk assessments the most commonly used impacts are changes in behaviour, malformations and growth problems, birth defects, impaired reproduction and death of the species affected.

The exposure assessment begins with the estimation of residue concentrations in the environmental compartments. This can be done by measuring the actual concentrations in soil, water, sediments, air, etc. or by using models as the fugacity mentioned above. The amount of residues in the environment is by far the most important element in any exposure assessment, even more than the toxicity of a chemical, because "the dose makes the poison". However, the availability of the residues is also necessary to correctly estimate the exposure to non-target organisms. This availability depends on the persistence of residues in each of the environmental compartments, on their ability to accumulate in tissues of organisms, and finally on the probability of being affected by such residues.

The toxicity assessment makes use of the toxicity data available. These data are compiled in databases (e.g. AQUIRE by the US EPA) which give the lethal doses required to kill 50% of a tested population ( $LD_{50}$ ) or the lethal concentration ( $LC_{50}$ ) required to achieve the same endpoint in aquatic organisms. The data refer usually to a few surrogate species tested in the laboratory (rat, rabbit, quail, duck, trout) and very rarely in field conditions, perhaps due to the many difficulties involved in measuring such endpoints in other species. While there is sufficient information available for most old chemicals, scarce and often non-relevant data are found for new chemicals, making the toxicity assessment difficult or impossible in some instances.

The toxicity assessment can be done at three levels: i) toxicity to a single non-target species (e.g. humans); ii) toxicity to a taxonomic group of organisms (e.g. fish, birds); and iii) toxicity to an entire ecosystem. Commonly, the toxicity to a given species is extrapolated from the available  $LD_{50}/LC_{50}$  of the most similar surrogate species by calculating a toxicity equivalent (TE) per body weight. For the latter two levels, several statistical expressions can be used to estimate the toxicity of a chemical to such sets of animals, plants or both together. For instance, in a group of organisms of the same taxon the geometric mean of the individual toxicities to each species is considered the

most realistic approach (Solomon, 1999). Toxicity to ecosystems requires more elaborate procedures, which are described below.

Finally, the risk assessment is concluded by weighing the exposure against the toxicity and can be quantified as in the so-called quotient model (Urban and Cook, 1986)

$$\text{Risk} = \frac{\text{Exposure}}{\text{Toxicity}} = \frac{\text{Concentration (mg/kg)}}{\text{LD}_{50} \text{ (mg/kg)}}$$

According to the above expression, a risk value higher than 1.0 indicates that more than half the population of a certain species can be killed by the corresponding concentrations of a chemical found in the environment in or around a cotton farm. Although the quotient model can only be applied to single species or to a taxon, calculation of risks as exposure/toxicity is valid and equally applicable to ecosystems as well.

### ***Relative risk to ecosystems***

Quantifying the risk for individual chemicals is one thing; comparing the risk amongst several pesticides applied onto the same cotton farm is another. Both estimates and comparisons are possible when using expressions of relative risk, as is the case with the Ecological Relative Risk (EcoRR) methodology developed in the CRC research program 1.1.5. The EcoRR method estimates the exposure of a chemical as the product of the mass (M) of its residues in a compartment, its probability of exposure (P), its half-life ( $t_{1/2}$ ) in that compartment and a bioconcentration factor (BCF) in animal tissues

$$\text{EcoRR exposure} = M \times P \times t_{1/2} \times \text{BCF}$$

where  $M$  = concentration (mg/kg)  $\times$  volume of compartment ( $\text{m}^3$ ). The toxicity term may be the toxicity to a taxon, but it is usually the toxicity to the whole ecosystem, which is calculated as the weighted average of all taxa toxicities taking into account the number of species present in each taxon

$$\text{Toxicity to ecosystem} = \frac{\sum (n\text{LD}_{50j})}{N}$$

where  $n$  is the number species belonging to the taxon  $j$ , and  $N$  the total number of species ( $=\sum n$ ) in the ecosystem. This expression ensures the  $\text{LD}_{50}/\text{LC}_{50}$  of each taxonomic group are weighed by the biodiversity of the ecosystem for which the risk assessment is being done. The quotient of EcoRR exposure and toxicity to ecosystem renders a relative value of risk for each chemical and compartment, the total EcoRR being the addition of compartmental EcoRR scores

$$\text{EcoRR} = \sum \text{EcoRR}_i \quad \text{for all compartments } i.$$

The EcoRR methodology allows comparisons between two or more pesticides applied in the same environment, and it can be estimated for affected areas within or outside the cotton farm. In order to compare the relative risk amongst pesticides, a ranking of EcoRR scores is needed, i.e. Fig. 31.

High risk	$\text{EcoRR} > 100$
Medium risk	$10 < \text{EcoRR} < 100$
Low risk	$1 < \text{EcoRR} < 10$
Negligible risk	$\text{EcoRR} < 1$

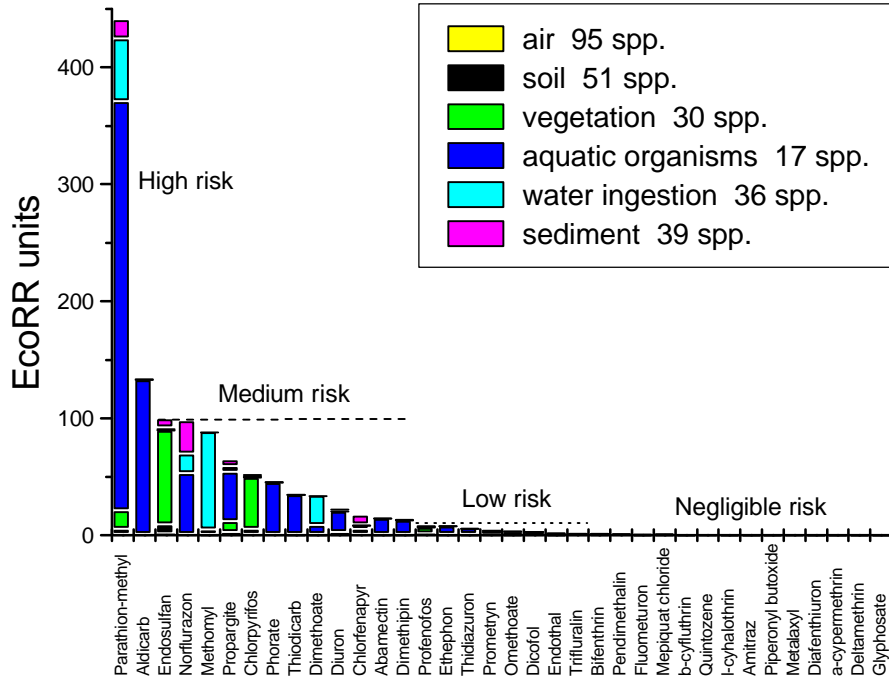


Figure 31. On-farm relative risk of 36 pesticides applied to a cotton farm

### Implications for farm management

In managing pesticides there are three logical steps to reduce any adverse environmental impacts

- i) minimise pesticide input
- ii) contain the pesticide to the application site, i.e. minimise drift and runoff spills
- iii) select pesticides with minimal environmental risk

The first and third steps have been discussed above. As for the second step, an appropriate farm design is essential. Some key points to be addressed in this regard are:

1. *Buffer zones.* The 40 metres buffer zone recommended in the past (EPA, 1995) has been extended to 1500 m downwind in the case of endosulfan (NRA, 1999; AgrEvo, 1999), since the old buffer only captures 50% or less of the total drift. There is no reason why other aerially applied chemicals should not follow the same rule, given that drift is an entirely physical phenomenon independent of the chemical characteristics of a compound. This extended buffer zone implies that cotton farms should not be allowed in the proximity of grazer land, water courses, wetlands, etc. at least on the prevalent downwind directions. Besides, ULV formulations can drift much further than EC formulations, therefore extending the risk over larger areas around the cotton farm. For this reason the NRA has recently banned the use of ULV endosulfan to avoid drift onto grazing pasture nearby.

2. *Tree/shrub barriers.* Whenever a cotton field is within 1500 of a sensitive area (i.e. river, livestock farm) a tree or shrub barrier should be planted to avoid drift onto such areas. Vegetation is an excellent adsorbent of pesticides, and a good remediating agent since foliage can degrade many chemicals.

3. *Levee banks.* Ideally no runoff water should leave the farm, and this can be achieved by building a levee bank around the farm. Current irrigation systems are designed only to recycle the

irrigation runoff. Levees, however, can hold storm runoff within the farm boundaries and also prevent flood waters from coming in. Both storms and floods are unpredictable in nature, impossible to avoid, and carry away large quantities of soil loaded with pesticide residues which contaminate neighbouring land and rivers downstream.

4. *Water reservoirs.* Another solution to contain storm runoff is to reserve some spare land on farm that may act as a water runoff buffer whenever there is a large storm. Such water reservoir could be fallow fields located in the lowest part of the property, thus capturing the runoff by gravitation. Furthermore, lower land is not very suitable for cotton due to waterlogging.

5. *Remediation.* The only effective system to eliminate residues is to degrade them. This can be achieved in several ways, such as passing the outflows through vegetative strips (e.g. croplands, grassed waterways, stubble) or through detoxifying materials (e.g. crushed coal), and building artificial wetlands on one side of the return drains to stimulate degradation by a combined effort of aquatic plants and microorganisms. Currently, there is a CRC research project on wetlands remediation that eventually will help clean up of tailwaters on cotton farms.

6. *Soil type.* Within the limitations of a given area, new cotton developments should avoid lighter sandy soils because they are prone to leaching of most herbicides. However, in order to avoid leaching it is easier to choose chemicals with no such tendency, since even heavy clay soils allow infiltration of most soluble compounds, though at a slower pace.

7. *Mulching.* New developments in northern Australia are showing that covering the cotton beds with grass mulch has a significant effect on reducing leaching and stimulating the degradation of chemical residues, apart from avoiding soil and nutrient losses by intense runoff and increasing beneficial insects (Yeates, pers. comm.). Obviously, the same practice could be applied elsewhere.

## Conclusion

A summary of the residue data in the riverine environment shows that endosulfan, atrazine and to a lesser extent other herbicides, are the most commonly occurring pesticides in river systems in cotton-growing areas (Muschal, 2000). Atrazine is no longer used by the cotton industry and consequently, priority was placed on obtaining a clear picture of endosulfan's persistence, fate and environmental impact on the CRC research, since residues of other recommended insecticides are only occasionally detected in those rivers.

The research data on endosulfan show that it disappears quickly from plants and soil largely by volatilisation. Soil microorganisms, microfauna and plants convert some of the endosulfan to endosulfan sulphate. The sulphate is moderately persistent in plants and soil, where it is slowly degraded to non-toxic compounds. Nearly all the residues on cotton plants disappear a month after spraying, although endosulfan sulphate may persist for a long time on dried plant material (cotton trash and contaminated pasture). If used repeatedly, endosulfan and endosulfan sulphate residues remain in the soil during the entire growing season. However, there is little carryover of either endosulfan or the sulphate in farm soils from one year to the next. Residues from other insecticides have been detected occasionally, but insufficient research means there is no evidence of significant build-up of these chemicals in cotton soils.

Chemical monitoring has shown that endosulfan residues are commonly present in stream water adjacent to, and downstream from cotton growing areas, often in excess of the guidelines for aquatic ecosystems. Our research data also show that this contamination with endosulfan is occurring mainly through aerial transport (droplet drift, contaminated dust, volatilisation) and by erosion of

contaminated soil following intense rainfall. Irrigation runoff, however, only contributes to riverine contamination whenever runoff spillages occur, if any. Thus, environmental contamination by endosulfan or other pesticides used in cotton production could be contained by firstly reducing drift, and secondly preventing storm and irrigation runoff from entering the riverine systems. A variety of containment methods could be used, but eventually the most effective way to eliminate such residues is by enhancing their bio-degradation on farm.

Although pesticides residues could be chemically detected in water and sediment using highly sensitive analytical methods, biomonitoring studies have so far provided no firm evidence that endosulfan residues in water are causing substantial impact in stream ecosystems (Brooks, 1998). However, long term impacts on biodiversity remain unknown, and the cotton industry cannot be complacent with this lack of knowledge but rather should adopt a cautious attitude in regard to pesticide usage.

## BEST MANAGEMENT PRACTICES

The results of this research program provided many lessons of environmental significance. Most importantly, a number of recommendations were made and incorporated in the Australian Cotton Industry Best Management Practices Manual (Williams, 1997). In addition, it has been possible to develop protocols that apply to a broad range of chemicals needed by the cotton industry.

### Recommendations

Specific recommendations for best practices that arose from this study on endosulfan were aimed at i) at minimising the pesticide load, and ii) containing all pesticide residues on the site of application and reduce the vulnerability to further runoff off-farm.

*Develop strategies to minimise the pesticide load on cotton fields.*

In general, a reduction of pesticide usage is desirable not only to reduce environmental risks but also to avoid resistance development in the target pests. Strategies that should be considered to minimise loads include:

- minimise the number of pesticide applications. This may be achieved by careful monitoring of pest pressure (i.e. using packages such as ENTopak developed by the CRC), so insecticides are maximised in efficiency and minimised in quantity. For herbicides, reducing the total number of applications to one/two before planting and another after planting may be sufficient to achieve the desired results (Roberts, 1997). The bonus of this kind of management is a smaller bill for the growers!
- avoid insecticide sprayings onto bare soil. Within the current pesticide management strategy (see Fig. 1) endosulfan and dicofol are applied early in the season, at a time when cotton fields are almost bare. In these conditions most endosulfan goes onto the soil, dissipating more slowly and being prone to removal by erosion. The introduction of transgenic Ingard cotton will help reduce the early season sprayings up to 25-30% of the areas planted to cotton. In conventional crops, alternative strategies based on IPM should replace the need for early sprayings;
- apply the principles of integrated pest management (IPM) to encourage biodiversity of insects and specially of beneficial predators, which reduce the onset of pests in cotton fields. Several methodologies are available such as food-sprays (Mensah and Singleton, 1998), plant buffer zones to grow beneficials, mulching to protect beneficials from insecticide sprays, etc;
- increase the interval between sprayings of the same chemical. The intervals normally used for endosulfan (10-15 days) are not sufficiently long to allow for a substantial degradation of its residues in soil. While the requirements for pest control may limit flexibility, this principle should be kept in mind wherever alternative strategies for pest control exist (e.g. IPM).

Spreading pesticide residues more widely over the farm (i.e. building roads using sediments from the taildrains) implies a greater contaminated area for soil erosion, raising the likelihood of residues going off-farm in storm runoff.

*Containing pesticide residues on farm*

The two main causes for transport of residues off-farm, namely drift and runoff, need to be tackled using an array of different strategies. Reducing drift onto areas off-farm may be possible by carefully following the specific directives given to this effect in the BPM, but it is still unavoidable in most existing cotton farms due to their layout.



As for the irrigation runoff, relevant strategies developed as part of this research which were included in the Farm Simulation Model (Tuite, 1996) for irrigation control, are summarised below:

- avoid irrigating soon after an application, to reduce pesticide loads in runoff to a minimum, particularly in the early irrigations because of the higher loads found in soil (see Fig. 10);
- reduce erosion by using flat furrow gradients particularly near and in tail drains, because sediment load is directly related to velocity of flow (Silburn *et al.*, 1998);
- minimise cultivation to reduce erodibility during storms, but minimum tillage herbicide treatments should be monitored carefully for environmental impacts;
- reduce erosion by retaining stubble and other vegetation on cotton fields. Stubble prevents sealing of the soil surface and improves soil infiltration, thus reducing runoff during irrigations and in storms (Silburn *et al.*, 1998);
- recirculate all tail waters on farms and provide the maximum capacity for their retention in ponds or depressions during storms;
- build storage dams with sufficient capacity to recycle as much as possible all runoff water within the farm;
- develop Farm Environmental Plans, including ameliorating practices such as strategic location of fallow fields to retain and receive storm waters, directing storm runoff away from the riverine system;
- schedule irrigations by careful monitoring of soil moisture conditions. In this respect, careful attention should be paid to weather forecasts to avoid irrigating just before storms.

Ponding of water may help degradation in certain pesticides. However, it does not encourage endosulfan dissipation, as the half-lives of this pesticide in the pond experiment were found to be similar to those in soil, and there was a 50% deposition as sulphate on the bottom floor. Hydrolysis in ponds could be fostered by alkaline treatment (Kimber *et al.*, 1996), since endosulfan is quickly degraded under high pH, or by bioremediation with mixed microbial cultures or enzyme preparations (Russell *et al.*, 1998), possibly including cyanobacteria.

Although flocculants could be useful tools for reducing pesticide levels in runoff waters by precipitating the particulate matter, their applicability is doubtful as they may introduce new environmental hazards and cost money. Also, improved engineering design of the field outlets and return drains may be needed to properly manage flocculant use.

## LEGAL REQUIREMENTS

The most recent legislation regarding pesticides are the Pesticides Act 1999 (NSW) and the Chemical Usage (Agricultural and Veterinary) Control Act 1988 (Qld). Both Acts require that pesticides are used according to instructions on the label or permit and that for each use actions are taken to ensure appropriate application. Considerable penalties apply for breaches of the Act, and it is desirable that strong policies like this remain in order to safeguard responsible pesticide use (Farrier, 1993).

The Pesticides Act 1999 aims to reduce the risks associated with the use of pesticides to human health, the environment, property, industry and trade. It also aims to promote collaborative and integrated policies for the use of pesticides, introducing many new and strengthened provisions to significantly improve the management of pesticides. Under the new Act, cotton growers and applicators should be aware that

- it is an offence to use a pesticide in a way that causes injury or likely injury to another person, damage or likely damage another person's property, or harm to a non-target plant or animal. On-farm exceptions apply. The maximum penalties for these offences are \$60,000 for an individual and \$120,000 for a corporation;
- it is illegal to possess, prepare for use or use a pesticide in NSW unless it is registered by the NRA or covered by an NRA permit. Prosecution would occur where there was an indication of intent to use an unregistered pesticide;
- it is illegal to disregard the label instructions on a registered pesticide. You must read all the label -not just the rate of application - or have it read to you before using any pesticide, and then carefully follow all the instructions on the label;
- storing pesticides in unlabelled containers such as soft drink bottles or open buckets may pose a real danger to human health, especially to children. The new Act requires that a person must not keep a pesticide in a container that does not bear its approved label;
- a pilot is not allowed to discharge pesticide from an aircraft within 150 metres of a dwelling, school, factory or any other public place without the written permission of the occupier. Roads, travelling stock reserves and State Rail land are excluded from the definition of public places.

The Waste Disposal Act 1970 (NSW) prohibits any person from polluting waters unless that person holds a licence from the EPA to discharge pollutants to receiving waters. This Act is the main legal requirement that guides the practices of the cotton industry with respect to pollution of riverine environments. EPA policy has been not to grant licences for return flows from irrigation farms. Under the Act, "waters" are defined as "any river, stream, lake, lagoon, swamp, wetlands, unconfined surface water or artificial water course, dam or tidal waters (including the sea), or part thereof, and includes water stored in artificial works, water in water mains, water pipes and water channels, and any underground or artesian water, or any part thereof". Any person who contravenes the provisions of the Act is guilty of an offence against the Protection of the Environment Operations Act 1997, for which heavy penalties apply.

## THE FUTURE

The CRC research has provided valuable data on the persistence, transport and impact of endosulfan and, to a lesser extent other pesticides used in cotton production. This information helps placing the pesticide “problem” in perspective relative to other environmental impacts. Also, it has demonstrated how differently each pesticide behaves in the environment, and finally improved farm management practices directed toward better containment and degradation of pesticide residues have been acknowledged.

### Industry directions

New technologies combined with IPM are seen as the solution to reduce the reliance of the cotton industry on pesticides. While their implementation may take some time, the industry must recognise the threefold benefit they bring i) to the crop by improving the pest-predator balance; ii) to the growers by reducing the operational cost; and iii) to the environment by reducing the pesticide residues and consequently their impact on ecosystems. Amongst the most recent developments in the industry, the benefits from the introduction of transgenic (GM) cotton and the use of attractants and pheromone traps are briefly outlined below.

#### *The impact of transgenic (Bt) cotton*

The introduction of Ingard<sup>®</sup> cotton expressing a *Bacillus thuringiensis* toxin (Bt) provides a unique opportunity to minimise the environmental impact from cotton pesticides. The performance of Ingard<sup>®</sup> cotton in the three seasons prior to 1999 show there is a substantial reduction in the use of endosulfan (70-85% reduction) and other insecticides sprayed early in the season, as well as synthetic pyrethroids (30-50%) and organophosphorous insecticides (15-30%) used in mid or late season respectively. About 50% of these sprays were directed to control heliothis pests.

Currently, about 10% of cotton crops are Ingard<sup>®</sup> cotton, with the prospect of increasing the area planted up to 25% of the total cotton growing area in Australia. The proportion of Ingard<sup>®</sup> and conventional cotton cannot be increased due to the need of providing refuges for heliothis pests in order to avoid resistance development (Fitt, 1997). This implies that the long-term success of Ingard<sup>®</sup> cotton is by no means assured as the likely development of insect resistance in the coming years may render the current transgenic varieties of little value.

From the economic point of view, the average combined cost of applied pesticides and license fee for Ingard<sup>®</sup> cotton was \$90 lower per hectare than the average cost of applied pesticides for conventional crops in the 1998-99 season. In previous years, yields between conventional and Ingard<sup>®</sup> crops were estimated as similar, but in 1998-99 an average 7.5% less yield across valleys was measured. At present, there is no explanation to account for these differences in yield, but obviously the energy required by the plant to produce Bt toxins must be detrimental for yield performance. This means the growers may get just a balanced bill, but the variability observed amongst individual farms ranged from a benefit of \$422 per ha in central Queensland to a \$325 per ha cost in the Gwydir valley (Pyke, 1999).

The great winner, however, is the environment, particularly in relation to endosulfan and other early season insecticides. Preferential planting of *Bt* cotton in environmentally sensitive areas (e.g. near rivers, wetlands and adjacent to pasture) could have a drastic effect in reducing endosulfan residues

in riverine systems or in neighbouring grazing land. It is recommended that the management of transgenic cotton be carefully integrated with strategies for chemical pesticide management, to take the best advantage possible for positive environmental outcomes.

### ***Herbicide-resistant cotton***

A contrasting situation exists with respect to the possible introduction of transgenic herbicide-resistant cotton. Such technology could involve many herbicides, starting with the already available RR cotton for glyphosate, and followed by GM varieties resistant to bromoxynil - which is already available in USA - and 2,4-dichlorophenoxyacetic acid (2,4-D). However, the availability of this kind of transgenic cotton could result in increasing herbicide use and cause greater environmental impacts (as well as litigious conflict regarding damage to other crops) if not carefully managed. For this reasons, the strategy discussed previously in this report designed to reduce and prevent environmental impacts from herbicides should be applied with preference to using GM herbicide-resistant cotton.

### ***Integrated Pest Management (IPM)***

A pest management program that requires a combination of all techniques - cultural, biological, genetic and chemical -, and is ecologically and economically acceptable to both the producer and the consumer, is called Integrated Pest Management or IPM. The benefits of IPM touch all facets of society. Growers benefit from reduced production costs, lower risk from pests, less exposure to pesticides and the development of a more sustainable agricultural industry. The environment benefits as environmental contamination and secondary effects on non-target species are avoided or reduced, this leading to increased biodiversity and sustainability in the ecosystems. The general public also benefits by the reduction in health hazards. Finally, the chemicals produced by chemical companies may have a longer useful life as the development of resistance can be slowed.

The primary aim of IPM is to protect crops from significant damage while minimising pesticide use. Available techniques include predators and parasites (beneficials), cultural methods, pest-resistant cultivars and pest control products such as attractants and pheromone traps. Pesticides are utilized only when pest populations exceed economically acceptable thresholds.

To achieve the primary aim, growers must define pest thresholds - i.e. the amount of injury that could result in a crop loss that is greater than the cost of control. Thresholds are influenced by crop growth stage, days to harvest, other pests, presence of beneficial organisms, market price, weather and pesticide costs. In this regard, guidelines provided by authorised bodies are often the result of years of experience, but it is up to the grower's discretion to determine when control is needed. Regular sampling, accurate identification of a pest's stage, good weather information, and clear and concise record keeping are the tools required to run an effective IPM.

Although there are numerous pesticides registered for controlling pests, only a few are compatible with IPM. Apart from being effective for the target pest, these pesticides should be of little toxicity to beneficial insects, not inducing pest resistance, and having little or negligible risk to the environment. Aware of this, chemical companies are now producing pesticides that can be used in IPM, which inevitably will replace in the future most of the products that are currently available. Besides, natural and biological products, supported by modern biotechnology, play an important role in improving and optimizing IPM. Often, biological agents provide a number of novel modes of action that cannot be achieved by chemistry alone. In contrast to the competitive and declining business of plant protection chemicals, biocontrol products are often perceived safer pest controls with

lower investment and a market growth of 5-10% annually in short to mid term (Voss and Mifflin, 1994). For this reason, some multinational chemical companies are investing a great deal in the development of new strains of *Bacillus thuringiensis*, or the marketing of new products like *Pseudomonas* spp. for the control of *Rhizoctonia solani* in cotton. For instance, control of pink bollworm using pathogenic nematodes (*Steinernema riobravis*) sprayed with ground-rig nozzles produced a 19% increase in cotton yields in Texas (Gouge *et al.*, 1998).

Other novel biocontrol products include pheromone/insecticide combinations, like Sirene (gossyplure and cypermethrin) which is being used against the pink bollworm (*Pectinophora gossypiella*) in Egyptian cotton (Nassef *et al.*, 1999). In addition to reducing the amount of insecticide per application by a factor of six, Sirene treated fields are significantly less infested and produce 10-23% higher yields than those treated with cypermethrin alone (Voss and Mifflin, 1994).

Disruption of mating using pheromone luring baits and traps in combination with small doses of insecticides, have proved effective in controlling pests in fruit trees (Chen *et al.*, 1999), rice (Tatsuki *et al.*, 1999), tea, coffee and many horticultural crops. The same technique has been tried in cotton, where a number of factors (e.g. temperature, light and behaviour) have been identified for obtaining good pest control (Rajaram *et al.*, 1999). The distance between pheromone sources, however, is the most critical factor determining success (Kehat *et al.*, 1999), and transfer of this technology to cotton is currently hampered by the large size of the Australian cotton fields. The advantage of this technology lies in its specificity, targeting only the pest species under control while having no effect on other species such as beneficial insects. Moreover, no resistance mechanisms are envisaged unlike in the case of pesticides.

Apart from sex pheromone, other chemicals are being investigated as possible attractants of pests including plant extracts and synthetic blends (Del Socorro *et al.*, 1999). Such compounds, whether natural or synthetic, are usually species or group specific and mixtures could be applied to target several pests at the same time (Du, 1999).

Although biocontrol products may look inferior to chemicals in terms of quickness, degree, duration and reliability of performance, they play an important role in softening treatments, delaying insect resistance and reducing enormously the amount of pesticide residues on farm and surrounding environment. Together with pest-resistant plants, such as *Bt* cotton (Ingard®), they will emerge as products that chemical companies (e.g. Shin-Etsu Chemical Co. Ltd) can manufacture to replace their current pesticide market.

### Research directions

Having outlined the future of the cotton industry in regard to pest control, it is now clear that pesticides will be relegated to a second line of defence in the new millenium. The variety of techniques and non hazardous products such as pheromones and attractants to be used in controlling cotton pests will ensure that insect populations are checked before they reach pest proportions. More research, however, would need to focus on weed control without herbicides. Agronomists must realise that the environmental effect of herbicides applied to agro-ecosystems could have disastrous consequences in the long term (Morrison and Meslow, 1983), since herbicides are usually persistent, water soluble (hence their tendency to leach), non selective and effective on a wide range of plant species.

With this in mind, pesticide research should concentrate on remediation of residues and prevention of risks associated with herbicides and new chemicals. As modelling risks need to be validated with some field data on actual residue concentrations, the development of cheaper and reliable analytical methods for detection and measurement of pesticides will be desirable.

### ***Remediation of pesticide residues***

The most urgent need within the cotton industry is to clean up the residues remaining on farm, whether in field or in irrigation systems. It is true that some off-farm contamination by drift cannot be avoided at the moment unless spraying is banned, but as this research has highlighted the amount of pesticide residues leaving the farm is minimal compared to the levels found on farm. Residues on farm irrigation systems, on the other hand, have an adverse impact on the surrounding fauna that comes to the water storages and channels for feeding or drinking (Whyte and Wurster, 1989).

Some research on remediation techniques has been carried out in the past, but there is still plenty of work to do to achieve workable systems that eliminate pesticide residues. Such systems need to be affordable to the grower, simple to operate and maintain, preferably be based on biological processes (bioremediation) that are self-reliant and require low inputs. For instance, bioremediating systems should not require the use of additional chemicals that may be an economic burden to the grower. Although micro-organisms are the most effective biodegrading agents, a bioreactor alone may not be enough to cope with the cocktail of residues found in tailwaters of irrigated cotton farms.

A current research project funded in part by the Cotton CRC is looking at building small size artificial wetlands as an option to filter the runoff effluent (from irrigation and storms) as a first step for pesticide clean up. A further step will involve the use of a bioreactor where a thorough microbial degradation of the remaining residues takes place. This integrated system is conceptually based on proven technologies such as those used for sewage and waste treatment worldwide, though its application to agricultural farms is novel. Trials on small scale need to be set up on existing farms of average size, and a protocol for application and transfer of this technology to larger cotton farms and other agricultural industries will be produced.

Thus, by cleaning their own residues, cotton growers will be demonstrating they are responsible toward the environment.

### ***Modelling to prevent risks***

Risk assessment of existing or new pesticides can be done by modelling rather than by performing expensive monitoring programs, since the data collected on fate and transport of cotton pesticides in the CRC program plus the information available in the literature are sufficient for assessment of most environmental impacts, with exception of leaching perhaps. However, as models depend entirely on reliable data for specific environments, some laboratory experiments using soils and water from Australian cotton regions may be required to validate the information already available on chemicals. Assessment of risks using models will save time and resources, allowing the prevention of hazards whenever a new chemical is approved for use in cotton.

Unfortunately, all the previous research was done after problems have become apparent in the environment. As a result the cotton industry has a less than desirable public relations image. It is a wiser policy to prevent such problems from occurring in the first place, and that is where modelling can fulfil an important role (Connolly *et al.*, 1998).

### *New monitoring tools*

It was also mentioned above that cheaper and readily available techniques for pesticide residue analysis are being sought. The use of immunoassays in pesticide residue analysis is being accepted worldwide, despite some skepticism from analytical laboratories, but ELISA kits are used mainly in monitoring of pesticide residues in produce (Skerritt, 1998).

There are currently ELISA kits available in Australia, some of which have been developed by the CSIRO (Table 8).

**Table 8. Pesticide immunoassay developed at CSIRO Plant Industry**

Compound	Food matrices	Environmental matrices
<b><i>Organophosphates</i></b>		
fenitrothion	grain, cereal foods	
parathion	rice, fruit, veg	water
methyl-parathion	rice, fruit, veg	water
chlorpyrifos		water, soil
chlorpyrifos-methyl	grain, cereal foods	
pirimiphos-methyl	grain, cereal foods	
diazinon	fruit juices	water, lanolin
<b><i>Organochlorines</i></b>		
cyclodienes	fruit, veg, fatty foods	water, soil
endosulfan	fruit, veg, grain, fats	water, soil
DDA/DDT	milk, fruit, veg, grain	soil
DDE/DDT	milk	water, soil
dicofol	fruit	
<b><i>Synthetic Pyrethroids</i></b>		
bioresmethrin	grain, cereal foods	
phenothrin	grain, cereal foods	
deltamethrin	grain	water, soil
cypermethrin	grain	water, soil
cyhalothrin	grain	water, soil
<b><i>Insect growth regulators</i></b>		
methoprene	grain, cereal foods	

As new chemicals are introduced in the cotton industry, development of their specific immunoassays is a task that usually takes several months or longer. Once the specific antibodies have been raised and tested, a few laboratory trials to test matrix effects on soils, foliage, and river water, can be done in a short time. Then, it is feasible to establish an analytical protocol that can be applicable in field monitoring programs.

Finally, research on new biosensors with the aim of providing more sensitive, accurate and affordable methods of residue analysis is taking place. Several biosensors have already been developed and tested for environmental matrices (Nunes *et al.*, 1999; Skládál *et al.*, 1999), and research in this field looks promising.

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# APPENDICES

## APPENDIX 1 Cotton pesticides and their application rates

Field application rates, in litres/kilograms per hectare, of pesticides registered for use on cotton crops and irrigation channels in Australia.

COMPOUND	TRADE NAMES	RATE OF APPLICATION (L/ha or kg/ha)
<b>DEFOLIANTS</b>		
Dimethipin	Harvade	0.35-0.5
Endothal	Accelerate	1-2 (LC)
Ethephon	Arvest, Ethephon, Ethrel, Finish (+), Galleon, Prep	2.0-4.5 (480), 1.3-3.0 (720), 0.94-2.2 (1000)
Magnesium chlorate	Magsol	5-7 (SC)
Sodium chlorate	Atlacide, Leafex	11-16.5 (240), 11-22 (300)
Thidiazuron	Dropp, Dropp Ultra (+)	0.1-0.35 (WP)
<b>FUNGICIDES</b>		
Carboxin	Vitavax	0.005 (seed)
Metalaxyl	Apron XL	0.13 (G, EC, WP)
Quintozene	Chloroturf, Rhizoff, Terraclor	5-0.08 (seed)
Triadimenol	Baytan C (+), Baytan T (+)	0.005 (seed)
Fipronil	Cosmos, Regent	0.0625-0.125 (SC)
<b>HERBICIDES</b>		
Amitrole	Amitrole-T	Channel: 0.28-4.6/100 L (AC), 0.6-1.2/100 L (WP)
Atrazine	Atradex, Atragranz, Gesapax	Channel: 0.28-4.6/100 L (AC), 0.6-1.2/100 (WP)
Butoxydim	Falcon	0.12-0.18 (G)
Dicamba	Banvel, Cadence	Fallows: 0.5-1.4 (AC)
Diquat dibromide	Reglone, Spray-Seed (+)	Fallows: 1.5-3.0 (AC)
Diuron	Diurex, Diuron, Dropp-Ultra (+)	Channel: 20-140 (SC), 40-110 (WP), 13-80 (G) Field: 1.8-3.5 (SC), 1.1-2.2 (WP), 1-2 (G)
Fluazifop-P-butyl	Fusilade, Fusion	0.75 (LC)
Fluometuron	Fluometuron, Nutron, Cotoran (+), Bandit (+), Cotogard (+), Cottomix (+),	Channel: 22-110 (WP) Field: 1.8-7.2 (SC), 0.8-1.7 (WP)



Promo-Mix (+)			
Glyphosate	Glyfos, Glyphos CT, Glyphosate, Roundup, Touchdown, Weedmaster, Wipe-Out	Channel: 1.5-9.0 (AC) Field: 0.4-2.4 (AC)	
Halosulfuron-methyl	Sempre	0.065-0.130 (G)	
Haloxypop-R-methyl	Verdict	0.4-0.6 (EC)	
Imazapyr	Arsenal	Channel: 6.0 (AC)	
MSMA	Daconate, MSMA	3.1 (LC), 1.0-2.8 (EC)	
Norflurazon	Zoliar DF	2.3-4.2 (WP)	
Paraquat dichloride	Para-Di, Gramoxone, Spray-Seed (+)	Fallows: 1.5-3.0 (AC)	
Pendimethalin	Stomp	Channel: 4.5-9.0 (EC); Field: 1.1-4.5 (EC)	
Prometryn	Gesagard, Prometryn, Proton	1.1-4.5 (SC)	
Propaquizafop	Correct, Shogun	0.2-0.9 (EC)	
Pyriproxyfen	Staple	0.14 (WP)	
S-Metolachlor	Dual Gold	2.0 (EC)	
Sethoxydim	Sertin	1.0 (EC)	
Triclopyr-butyl	Garlon	Fallows: 0.08-0.16 (EC)	
Trifluralin	Treflan, Triflur, Trifluralin, Trifluralin Extra	1.4-2.8 (400), 0.93-1.87 (600)	
Cyclanilide	Finish (+)	3.0-3.7 (SC)	
Mepiquat chloride	Concorde, Ensign, Pix, Reward	0.25-1.00 (AC)	
PLANT GROWTH REGULATORS			
INSECTICIDES			
Abamectin	Agri-mec, Wizard	0.3-0.6	
Aldicarb	Temik, Touche	3.0-7.0 (G)	
Alpha-cypermethrin	Alpha-Scud, Dominex, Fastac	0.3-0.5 (EC), 2.0-3.0 (ULV)	
Amitraz	Amitraz, Opal, Ovasin	2.0 (EC, ULV)	
<i>Bacillus thuringiensis</i>	BtK, Conдор OF, Costar OF, Cybout, DiPel	0.45-0.90	
Beta-cyfluthrin	Bulldock, Bulldock-Dual	0.6-0.8 (EC), 1.9-2.5 (ULV)	
Bifenthrin	Talstar	0.6-0.8 (EC)	
Carbaryl	Bugmaster Flo	2.2 (SC)	
Carbosulfan	Marshal	20-40 mL/100 m row (EC)	
Chlorfenapyr	Intrepid	1.1 (EC, ULV)	
Chlorpyrifos	Chlorfos, Chlorpyrifos, Dursban, Instinct, Predator, Pyrinex, Strike-Out	0.3-1.5 (EC), 1.75-5.00 (ULV)	

* Chlorpyrifos-methyl	Reldan	1.0-2.0 (EC)
Cypermethrin	Cypermex, Cypermethrin, Scud, Sonic, Ripcord	0.3-0.7 (EC), 1.5-3.5 (ULV)
Deltamethrin	Ballistic, Decis, Decis Forte	0.5-0.7 (EC), 2.5-3.5 (ULV)
Diafenthiuron	Pegasus	0.6-0.8 (SC)
Dicofof	Kelthane, Miti-Fol	4.0 (EC)
Dimethoate	Dimethoate, Rogor, Roxion, Saboteur	0.3-0.5 (EC)
Disulfoton	Disulfoton	14.0 (G)
Emamectin benzoate	Proclaim	0.25-0.30 (SG)
Endosulfan	Endosan, Endosulfan, Thiodan, Thiodex	2.1 (EC), 3.0 (ULV)
Esfenvalerate	Hallmark	0.2-0.7 (EC), 1.0-3.5 (ULV)
Furathiocarb	Deltanet, Promet	0.022 (seed)
* Imidacloprid	Confidor, Gaucho	0.015-0.020 (seed)
Lambda-cyhalothrin	Karate	0.30-0.42 (EC), 2.5-3.5 (ULV)
Methidathion	Supracide	1.4 (EC)
Methomyl	Electra, Lannate, Marlin, Nudrin	0.5-2.4 (LC)
Monocrotophos	Azodrin, Monocron, Nuvacron	0.25-4.00 (AC)
Omethoate	Folimat	0.14-0.28 (EC)
Parathion-methyl	Folidol, Methyl-Parathion	0.7-2.8 (EC)
Phorate	Phorate, Thimet	6.0-17.0 (100), 3.0-8.5 (200)
Piperonyl butoxide	Pipbut, Piperonyl butoxide	0.25-0.45 (EC)
Pirimicarb	Aphidex, Pirimor	0.50-0.75 (WP)
Profenofos	Curacron, Profenn, Sabre	1.0-2.0 (500), 1.0-4.0 (250)
Propargite	Comite	2.5
Spinosad	Tracer	0.15-0.20
Tau-fluvalinate	Mavrik	3.3-5.0 (ULV)
Thiodicarb	Larvin, Semevin, Showdown	0.5-2.0 (EC, SC), 1.0-1.5 (AC)

\* Permit only

(+) Mixture with other chemicals

Key to formulations:

AC	Aqueous concentrate	P	Powder
EC	Emulsifiable concentrate	SC	Suspension concentrate
G	Granular	ULV	Ultra Low Volume
LC	Liquid concentrate	WP	Wettable powder

## APPENDIX 2      Degradation processes for cotton pesticides

	Chemical	Biological	Other
<b>Defoliants</b>			
Dimethipin	Slow hydrolysis		Decomposed by heat
Endothal	Conjugation in water to form salts	Aerobic microbial	Dehydration by heat
Ethephon	Alkaline hydrolysis	Microbial & plants	U.V. degradation (?)
Thidiazuron		Animals	U.V. degradation
<b>Fungicides</b>			
Carboxin		Animals & plants	U.V. degradation in water
Metalaxyl-M		Animals & plants	U.V. degradation in water
Quintozene	Alkaline hydrolysis	Microbial & plants	
Triadimenol		Microbial, animals & plants	
<b>Herbicides</b>			
Amitrole		Microbial & plants	
Atrazine	Strong acid/alkaline hydrolysis	Microbial & animals	
Butoxydim	Acidic hydrolysis	Aerobic microbial, animals & plants	
Dicamba		Microbial & plants	
Diquat dibromide	Alkaline hydrolysis		U.V. degradation in water
Diuron	Hydrolysis	Microbial, animals & plants	
Fluazifop-P-butyl	Alkaline hydrolysis	Animals & plants	
Fluometuron		Microbial & plants	U.V. degradation (?)
Glyphosate		Microbial & plants	Decomposed by heat
Halosulfuron-methyl		Microbial, animals & plants	
Haloxyfop-R-methyl	Hydrolysis	Microbial & animals	
Imazapyr			U.V. degradation (?)
MSMA			Oxidizing & reducing agents
Norflurazon		Animals & plants	U.V. degradation
Paraquat dichloride	Alkaline hydrolysis		U.V. degradation in water
Pendimethalin		Microbial, animals & plants	
Prometryn		Aerobic microbial & plants	U.V. degradation
Propaquizafop	Alkaline hydrolysis	Microbial & plants	
Pyrithiobac-sodium		Microbial & animals	U.V. degradation (?)
S-Metolachlor		Animals & plants	
Sethoxydim		Aerobic microbial & plants	U.V. degradation in water
Triclopyr-butotyl		Microbial & plants	U.V. degradation
Trifluralin		Microbial, animals & plants	U.V. degradation
<b>Plant growth regulators</b>			
Cyclanilide		Microbial	
Mepiquat chloride			Slowly decomposed by heat
<b>Insecticides</b>			
Abamectin		Microbial, animals & plants	U.V. degradation
Aldicarb	Oxidation	Microbial, animals & plants	
Alpha-cypermethrin	Alkaline hydrolysis	Aerobic microbial (?)	
Amitraz	Acidic hydrolysis	Aerobic microbial, animals & plants	
Beta-cyfluthrin	Alkaline hydrolysis	Aerobic microbial	Slow U.V. degradation

Bifenthrin		Aerobic microbial (?)
Carbaryl	Alkaline hydrolysis	Aerobic microbial, animals & plants
Carbosulfan	Hydrolysis	Microbial, animals & plants
Chlorfenapyr	Hydrolysis	Microbial & plants
Chlorpyrifos	Alkaline hydrolysis; catalysed by metal ions	Microbial, animals & plants U.V. degradation (?)
* Chlorpyrifos-methyl	Alkaline hydrolysis	Microbial & animals
Cypermethrin	Alkaline hydrolysis	Aerobic microbial
Deltamethrin		Microbial & animals U.V. degradation
Diafenthiuron		Microbial, animals & plants
Dicofol	Alkaline hydrolysis	Microbial, animals & plants U.V. degradation in water
Dimethoate	Alkaline hydrolysis	Microbial, animals & plants Decomposed by heat
Disulfoton	Alkaline hydrolysis	Microbial, animals & plants U.V. degradation in water
Emamectin benzoate		Microbial, animals & plants U.V. degradation in water
Endosulfan	Alkaline hydrolysis	Microbial, animals & plants
Esfenvalerate		Microbial, animals & plants
Fipronil	Alkaline hydrolysis	Microbial, animals & plants U.V. degradation in water
Furathiocarb	Alkaline hydrolysis	Microbial, animals & plants
* Imidacloprid		Aerobic microbial, animals & plants U.V. degradation in water
Lambda-cyhalothrin		Microbial, animals & plants Slow U.V. degradation
Methidathion	Alkaline hydrolysis	Microbial, animals & plants U.V. degradation
Methomyl	Alkaline hydrolysis	Microbial, animals & plants
Monocrotophos	Alkaline hydrolysis	Microbial, animals & plants Decomposed by heat
Omethoate	Alkaline hydrolysis	Microbial, animals & plants
Parathion methyl	Alkaline hydrolysis	Aerobic microbial & plants U.V. degradation in water; decomposed by heat
Phorate	Hydrolysis	Aerobic microbial, animals & plants U.V. degradation in water
Pyperonyl butoxide		Aerobic microbial & animals U.V. degradation in water
Pyrimicarb	Hydrolysis	Animals
Profenofos	Alkaline hydrolysis	Animals & plants
Propargite	Alkaline hydrolysis	Animals & plants
Spinosad		Microbial & plants U.V. degradation
Tau-fluvalinate		Aerobic microbial & animals U.V. degradation
Thiodicarb	Alkaline hydrolysis	Microbial, animals & plants U.V. degradation

\* Permit only

## APPENDIX 3      **Field half-lives of cotton pesticides**

Type	Compound	Trade names	Half-life (days)
<b>Defoliants</b>			
	Dimethipin	Harvade	104 - 149
	Endothal	Accelerate	7 - 21
	Ethephon	Arvest, Ethephon, Ethrel, Galleon, Prep	10
	Sodium chlorate	Atlacide, Leafex	180 - 1725
	Thidiazuron	Dropp	26 - 144
<b>Fungicides</b>			
	Carboxin	Vitavax	1 - 3
	Metalaxyl	Apron XL	30
	Quintozene	Chloroturf, Rhizoff, Terraclor	120 - 300
	Triadimenol	Baytan	110 - 375
<b>Herbicides</b>			
	Amitrole	Amitrole-T	14 - 28
	Atrazine	Atradex, Atragranz, Gesapax	16 - 77
	Butoxydim	Falcon	9
	Dicamba	Banvel	14
	Diquat dibromide	Reglone	1000
	Diuron	Diurex, Diuron	90 - 180
	Fluazifop-P-butyl	Fusilade, Fusion	14 - 28
	Fluometuron	Fluometuron, Flowable Fluometuron, Nutron	85 - 100
	Glyphosate	Glyphos, Glyphos CT, Glyphosate, Roundup CT, Touchdown, Weedmaster, Wipe-Out	47 - 174
	Halosulfuron-methyl	Sempre	18
	HaloxyfopR-methyl	Verdict	55 - 100
	Imazapyr	Arsenal	90 - 180
	MSMA	Daconate, MSMA	55 - 180
	Norflurazon	Zoliar DF	180 - 270
	Paraquat dichloride	Para-Di, Gramoxone	1000 E
	Pendimethalin	Stomp	90 - 120
	Prometryn	Gesagard, Prometryn, Proton	60 - 158
	Propaquizafop	Correct, Shogun	15- 26
	Pyrithiobac-sodium	Staple	36 - 60
	S-Metolachlor	Dual Gold	90
	Sethoxydim	Sertin	5
	Triclopyr-butotyl	Garlon	46
	Trifluralin	Treflan, Triflur, Trifluralin, Trifluralin Extra T	57 - 116
<b>Plant Growth Regulators</b>			
	Cyclanilide	Finish (+)	16
	Mepiquat chloride	Concord, Ensign, Pix, Reward	10 - 97
<b>Insecticides</b>			
	Abamecin	Agrimec, Wizard	28
	Aldicarb	Temik, Touche	30 - 70
	Alpha-cypermethrin	Alpha-Scud, Dominex, Fastac	13 - 30
	Amitraz	Amitraz, Opal, Ovasin	2
	Beta-cyfluthrin	Bulldock, Bulldock-Dual	30
	Bifenthrin	Talstar	26 - 125
	Carbaryl	Bugmaster Flo	7 - 28
	Carbosulfan	Marshal	2 - 5
	Chlorfenapyr	Intrepid	70 - 280
	Chlorpyrifos	Chlorfos, Chlorpyrifos, Dursban, Predator, Pynex, Instinct, Strike-Out	30 - 120

Cypermethrin	Cypermethrin, Cypermax, Scud, Sonic, Ripcord	30 E
Deltamethrin	Ballistic, Decis, Decis Forte	23 - 33
Diafenthiuron	Pegasus	1 - 1.4
Dicofol	Kelthane, Miti-Fol	40 - 100
Dimethoate	Dimethoate, Rogor, Roxion, Saboteur	7 - 16
Endosulfan	Endosan, Endosulfan, Thiodan, Thiodex	30 (alpha) - 87 (beta)
Esfenvalerate	Hallmark	88 - 280
Fipronil	Cosmos, Regent	50 E
Furathiocarb	Deltanet, Promet	10 E
*Imidacloprid	Confidor, Gaucho	70 E
Lambda-cyhalothrin	Karate	28 - 84
Methidathion	Supracide	3 - 18
Methomyl	Electra, Lannate, Marlin, Nudrin	30
Monocrotophos	Azodrin, Monocron, Nuvacron	30
Omethoate	Folimat	2.5
Parathion methyl	Folidol, Methyl Parathion, Parathion-Methyl	5 - 47
Phorate	Phorate, Thimet	2 - 14
Piperonyl butoxide	Pipbut, Piperonyl butoxide	14
Pirimicarb	Aphidex, Pirimor	7 - 234
Profenofos	Curacron, Profenn, Sabre	7
Propargite	Comite	49 - 98
Spinosad	Tracer	9 - 17
Tau-fluvalinate	Mavrik	12 - 92
Thiodicarb	Larvin, Semevin, Showdown	3 - 8

\* Permit only

+ Mixtures

E Estimated

## APPENDIX 4 Sorption and mobility of cotton pesticides

	<b>Sorption</b>	<b>Mobility / Leaching</b>
<b>Defoliants</b>		
Dimethipin	Weakly sorbed by soil particles	It has great potential for leaching if washed off the plants by storms.
Endothal		Highly mobile, but rapid degradation limits the extent of leaching if washed off by storms.
Ethephon	Fast binding to organic matter.	It has potential for leaching in sandy soils.
Magnesium chlorate	Remains in soil.	
Sodium chlorate	Remains in soil.	It has potential for leaching in sandy soils.
Thidiazuron	Some adsorption onto soils - remains longer under aerobic conditions.	Moderate mobility.
<b>Fungicides</b>		
Carboxin	Some adsorption onto soils.	Low to medium mobility.
Metalaxyl	Poorly adsorbed by soils.	Mobile, with potential for leaching.
Quintozene	Binds strongly to soil organic matter.	Some volatilisation. Very persistent. Immobile.
Triadimenol	Moderate to strongly sorbed by soil.	Tendency to leach in sandy soils. Persistent.
<b>Herbicides</b>		
Amitrole		Very mobile, with leaching to groundwater.
Atrazine	Some adsorption onto organic matter.	Mobile, with leaching to groundwater.
Butoxydim	Strongly sorbed in low pH soils.	Low mobility.
Dicamba	Weakly sorbed by soil particles.	Leaching restricted by rapid degradation.
Diquat dibromide	Binds strongly to clay.	Immobile.
Diuron	Some adsorption onto soils. Persistence depends on soil organic matter.	Mobile, with leaching potential.
Fluazifop-P-butyl	Binds strongly to soil organic matter. More persistent in cold-dry conditions.	Very low mobility.
Fluometuron	Weakly sorbed by soil organic matter. Persistent under dry conditions.	Prone to leaching.
Glyphosate	Strongly adsorbed by clay.	Immobile.
Halosulfuron-methyl	Weakly sorbed by soil particles.	Leaching restricted by rapid degradation.
Haloxypol-R-methyl	Binds to soil organic matter.	Low mobility.
Imazapyr	Weakly sorbed by soil particles.	Very mobile, with leaching to groundwater.
MSMA	Binds to upper soil layers, particularly in loamy soils. Persistent.	Low to medium mobility.
Norflurazon	Binds to soil under high pH.	Moderate mobility. Very persistent.
Paraquat dichloride	Strongly adsorbed by soil organic matter and clay.	Very persistent in soil and in the bottom mud of pools and ponds. Immobile.
Pendimethalin	Binds strongly to soil organic matter. Persistent.	Some volatilisation. Very low mobility.
Prometryn	Binds to soil and suspended sediments. Persistent.	Mobile, with possible leaching in sandy soils.
Propaquizafop	Binds strongly to soil organic matter.	Very low mobility.
Pyrithiobac-sodium	Weakly sorbed by soil organic matter.	Very mobile, with leaching in sandy soils.
S-Metolachlor	Some adsorption onto soils.	Mobile, with possible leaching in sandy soils.
Sethoxydim	Weakly sorbed by soil organic matter.	Mobility restricted by rapid degradation.
Trifluralin	Adsorbed by soil and organic matter. More persistent in neutral media.	Volatilisation occurs. Very low mobility.

## Plant Growth Regulators

Cyclanilide	Binds to soil organic matter.	Mobility restricted by rapid degradation.
Mepiquat chloride	Persistent.	Low mobility.

## Insecticides

Abamectin	Binds tightly to soil organic matter.	Immobile.
Aldicarb	Moderately persistent, but less in alkaline soils and aerobic conditions.	Very mobile, with leaching to groundwater.
Alpha-cypermethrin	Strongly bound to soils, sediments and organic matter (vegetation).	Immobile.
Amitraz	Strongly adsorbed by soil organic matter.	Immobile. Less persistent in acidic media.
Beta-cyfluthrin	Strongly bound to soils, sediments and organic matter (vegetation).	Immobile.
Bifenthrin	Strongly bound to soils, sediments and organic matter (vegetation).	Immobile. Persistent.
Carbaryl	Weakly sorbed by soils. More persistent in clay loams than in sandy soils.	Mobility restricted by rapid degradation.
Carbosulfan	Degradable, but the product (carbofuran) is moderately persistent.	Very low mobility.
Chlorfenapyr	Strongly bound to soil particles.	Very low mobility.
Chlorpyrifos	Strongly bound to soil particles. More persistent in acidic or neutral media.	Very low mobility. Metabolites more mobile.
Cypermethrin	Strongly bound to soils, sediments and organic matter (vegetation).	Immobile.
Deltamethrin	Strongly bound to soils, sediments and organic matter (vegetation).	Immobile.
Difenthiuron	Strongly adsorbed onto soil particles.	Immobile.
Dicofol	Adsorption is stronger in sandy soils	Very low mobility.
Dimethoate	Weak sorption, depending on silt content.	Leaching potential restricted by rapid degradation.
Disulfoton	Weak sorption to organic matter.	Low mobility.
Emamectin benzoate		Low mobility.
Endosulfan	Strongly bound to soil particles. The sulphate metabolite is persistent in soil.	Volatilisation occurs. Very low mobility.
Esfenvalerate	Strongly bound to soil organic matter. Very persistent.	Immobile.
Fipronil		Low mobility.
Furathiocarb	Strongly adsorbed onto soil particles.	Low mobility.
*Imidacloprid	Moderately persistent.	Mobile, with potential for leaching.
Lambda-cyhalothrin	Strongly bound to soils, sediments and organic matter (vegetation).	Immobile. Less persistent in alkaline media.
Methidathion	Poorly sorbed by soil.	Moderate mobility.
Methomyl	Low affinity for soil organic matter.	Very mobile, with leaching potential.
Monocrotophos	Weakly sorbed by soil particles.	Very mobile, with leaching potential.
Omethoate	Weakly sorbed by soil particles.	Low mobility. Metabolites are more mobile.
Parathion methyl	Binds strongly to soil organic matter. Persistent.	Very low mobility.
Phorate	Binds strongly to soil organic matter.	Low mobility.
Piperonyl butoxide	Binds strongly to soil organic matter.	Very low mobility.
Pirimicarb	Poorly sorbed by soil.	Mobile, with potential for leaching.
Profenofos	Binds strongly to soil organic matter.	Very low mobility.



Propargite  
Spinosad  
Tau-fluvalinate  
Thiodicarb

Strongly bound to soil organic matter.  
Strongly bound to soil organic matter.  
Strongly bound to soil.  
Sorption depends on soil type.

Moderate mobility. Persistent.  
Very low mobility.  
Immobile.  
Volatilisation occurs. Low mobility.