



## Cotton Pesticides in Perspective: Minimizing their Impact on Produce and in Riverine Ecosystems

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### ABSTRACT

*Despite measures taken to reduce reliance on chemicals (e.g. Ingard cotton), production of Australian cotton still involves significant inputs of pesticides, with the potential to contaminate other agricultural produce and riverine ecosystems. Since 1993, the environmental fate and transport of pesticides used in cotton growing have been extensively monitored to minimize their impact as chemical residues. This research has focused on endosulfan as the major insecticide applied on cotton farms, and as a model for other chemicals. Positive results of the research that can help provide more sustainable practices are:*

- *Information on field dissipation of endosulfan, in farm soils, surface water and on nearby pasture. In summary, dissipation of endosulfan from cotton fields occurred mainly by volatilization in the first 2-3 weeks after application; endosulfan isomers on cotton plants and in soils are quickly metabolized, with half-lives of 3-4 days. Two weeks after application, only 2-3 % of the amount applied in one spraying remained in the foliage. Unfortunately, there is some persistence of the metabolic oxidation product endosulfan sulphate in the field, with a 'half-life' in soil of about 100 days. However, by the start of the new growing season only 1-2% of the endosulfan applied remained on field as endosulfan sulphate, so there is little or no long-term accumulation.*
- *A study of the degradation of endosulfan on pasture showed that residues fell to acceptable levels within about 3-4 weeks, dependent on the distance from the line of spray application. Runoff waters contain 1-2% of total endosulfan transported or dissipated off field in one season, major storms accounting for 50% of this amount; the relative significance of lateral rather than vertical leaching of soluble chemicals in grey-cracking soils (Vertisols) is emphasized.*
- *Immunoassays (ELISA) provide rapid, inexpensive, field tests for pesticide residues, providing more comprehensive data-sets that allow decisions on the release of contaminated water and the assessment of the progress in remediation.*
- *Field research protocols needed to generate data for registration purposes have been developed.*
- *Significant progress towards safer use of pesticides in cotton growing, resulting from the preparation of a database indicating risk factors with specific pesticides and herbicides and a better understanding transport mechanisms. The adoption of better management practices that reduce these risks is already contributing to more sustainable cotton production.*

### Introduction

A major research program on "Minimizing the impact of pesticides on the riverine environment using the cotton industry as a model", funded by the Land and Water Resources Research and Development Corporation (LWRRDC), the Cotton Research and Development Corporation (CRDC) and the Murray-Darling Basin Commission (MDBC), was initiated in 1993. One goal was to determine the relative importance of different mechanisms of transport off-

farm, such as aerial transport (volatilization, drift and transport on dust) and surface runoff in irrigation and storms that often lead to contamination of rivers (Cooper, 1996). The management of drift and runoff provides the greatest scope for improvements. Concomitant research related to the fate, containment, remediation of cotton pesticides, the degradation of endosulfan drift on pasture and the development of simple field test kits for pesticides were funded by the CRC for Sustainable Cotton Production and the CRDC. This paper discusses the on-farm fate and

transport of pesticides, focusing on endosulfan as an insecticide of major significance in river contamination and as a model for the behaviour of other pesticides.

These studies sought to establish the current burden and seasonal profiles of chemicals in cotton-growing soils, runoff water and cotton plants, to determine the mechanisms and rate of dissipation and the extent of their transport to the riverine environment. Additional work was conducted to develop test kits (immunoassays) for pesticides used in growing cotton, for use in the field and to assist in decision-making regarding residues. The ultimate aim was to provide an accessible database on practical protective measures for use of chemicals. As a result, management decisions have been placed on a more secure basis, but the task of reducing environmental impacts remains a complex and challenging one (Kennedy *et al.*, 1997).

## Methods

Full details of the experimental methods used in this study will be published elsewhere (Kennedy *et al.*, 1997). However, for illustrative purposes, the following details are supplied.

In some cases, the study was integrated with studies on aerial transport by drift (N. Woods, University of Queensland, Gatton), volatilization (V. Edge and N. Ahmad) and transport on dust (J. Leys, NSW Land & Water Conservation). The studies included hydrological measurement of flows off the field, measuring all relevant parameters related to meteorology, soil, sediment and water properties. Initially, stratified block designs were employed for convenience of large-scale sampling of soil and plant material, to allow analysis with respect to sampling intensity and to determine any spatial or temporal variability in soil residues.

Foliage samples, a set of filter paper strips placed in the field on wooden slats and another set on aluminium plates 1 metre above the canopy were used to estimate the amounts of pesticide falling on both soil and canopy immediately after spraying. Plant cover of soil by the cotton foliage was calculated using a shadow technique to measure horizontal cover near noon and by measuring the height and width of plants on 1 metre long sections of 10 furrows. Standard sampling protocols were used for soil and water runoff sampling (Kennedy *et al.*, 1998a). Foliage was sampled on each occasion as nine whole plants, allowing the calculation of a pesticide load per plant and a chemical balance for the whole field. As the season progressed and the cotton plants grew, plants were separated for analysis into outer and inner leaves, stems and bolls.

A project on quality assurance involving analysis of selected field samples in two or more analytical participating laboratories was conducted (Kennedy *et al.*, 1998a). Gas-liquid chromatography (GLC) data were generated following solvent extraction of water

and soil samples. Analyses by three different laboratories (the Biological and Chemical Research Institute at Rydalmere, the NSW Department of Water Resources at Arncliffe and the Department of Natural Resources at Indooroopilly, Queensland) assessed their accuracy. A validation of immunoassays (ELISAs) for soil and water samples using CSIRO immunoassay kits for endosulfan (Lee *et al.*, 1995, 1997) was also conducted. This allows the analysis of many more field samples than is possible by GLC.

## Results and discussion

### *Analytical methods and quality assurance*

The project on quality assurance has shown that the three main analytical centres involved produced gas-liquid chromatography (GLC) data within acceptable limits of quality assurance (Kennedy *et al.*, 1998). Analytical work by the laboratories in Rydalmere, Arncliffe and Indooroopilly proved that confidence in the accuracy of the range of analytical results obtained during this program was justified. Validation of the immunoassays (ELISAs) for endosulfan in soil and water samples using CSIRO field test kits has been a great advantage (Lee *et al.*, 1997), allowing many more field samples to be analyzed for pesticide residues. The compromise is some loss of specificity (all cyclodienes yield positives) and inability to distinguish between the toxic isomers of endosulfan and endosulfan sulphate. However, non-toxic products such as endosulfan diol are not detected and the sensitivity of detection in soil of about 0.1 mg/kg (ppm) and a range for analysis of 0.2-50 µg/L (ppb) in water were ideally suited to the needs of this study. Agreement between the results obtained by gas chromatography and immunoassay for soil and runoff water was excellent ( $r_2 = 0.9$ ), using at least 10gms. of well-mixed soil for reliable analyses with extraction in 90% methanol.

### *Degradation rates on cotton fields*

The following research conclusions on endosulfan apply to a range of pesticides.

The initial dissipation of endosulfan (70%  $\alpha$ -isomer, 30%  $\beta$ -isomer) on cotton fields occurs mainly through volatilization of the  $\alpha$ -isomer in the first 2-3 weeks after application (70%), with an apparent half-life of only 2-3 days. Such volatilization is temperature-dependent and applications made near sun-down are likely to be more effective, reducing the need for future applications and environmental dissipation to the atmosphere. Other rapid dissipation of endosulfan occurs in run-off water, either by volatilization, or hydrolysis, particularly if the pH value is above 8.0.

- Unfortunately, persistence of endosulfan in the field occurs because of the formation of a toxic oxidation product, endosulfan sulphate, with a 'half-life' in soil of about three months and some remaining  $\beta$ -endosulfan that is more firmly bound

to soil organic matter, of shorter half-life (Fig. 1). However, by the start of the new growing season only 1-2% of the endosulfan applied remains on field as endosulfan sulphate, so there is little or no long-term accumulation.

- Endosulfan in cotton plants, including the sulphate, quickly breaks down, with half-lives of 3-4 days. In two weeks, only 2-3 % of the amount applied in one spraying remains in the foliage (Fig. 2). By contrast, similar studies on the insect growth regulator chlorfluazuron (Helix) using similar methods indicate only a low degree of dissipation over the same period.
- Despite its rapid dissipation from plants, small amounts of endosulfan with concentrations of up to 0.5 mg/kg (dry matter), remain in cotton plant tissues, even after harvesting, six months after spraying. The current general prohibition on feeding gin trash to stock is obviously a wise precaution, but the risk with specific pesticides is dependent on the rate of breakdown in plants.

#### ***Fate of endosulfan in soil: half-life***

Baseline data obtained from soil sampled on cotton fields invariably showed a low residual concentration of endosulfan at the commencement of each cotton season (less than 0.08 mg/kg, equivalent to 60 g/ha). Apparently there is a two-phase dissipation of endosulfan from soil, firstly the parent isomers present in the formulation ( $\alpha$ - and  $\beta$ -endosulfan) disappear mainly by volatilization and secondly, endosulfan sulphate forms in soil, reaching a maximum of about 0.2 mg/kg about two weeks after the final spraying.

Apparent half-lives for each of these two phases have been estimated from a large number of data points (Table 1), with mean values of about 4 days and 138 days for the two phases. The half-life in soil varied from field to field as the environmental conditions (time of day, temperature, wind speed, etc.) differed for each spraying. In general, the decline in  $\alpha$ -endosulfan concentration in soil by volatilization was much faster than that for  $\beta$ -endosulfan, whilst endosulfan sulphate was formed quickly as  $\alpha$ -endosulfan disappeared. On one field, the peak quantity of endosulfan sulphate represented about one-  
Figure 4 shows curves for endosulfan dissipation (Kennedy *et al.*, 1998b) for pasture samples taken at 10 and 100 m. from the flight line.

#### **Implications of results, uptake and adoption**

These results on the fate of endosulfan have significant implications with regard to environmental care in cotton farming. Although the dissipation of endosulfan by volatilization and degradation on foliage is relatively rapid, sufficient residues remain in plant material to pose a risk if plant residues are taken off-farm. Degradation of foliage on cotton fields is preferable to ensure pesticide breakdown on-farm.

fifth the total endosulfan applied in the three aerial sprayings. Statistical analysis (ANOVA) of the data for the stratified design by rows and columns (Kennedy *et al.*, 1998) indicated that there was no significant difference in concentrations of endosulfan residues between different strata on the field. Thus, aerial application provides an even spread of pesticide, and the rate of conversion to endosulfan sulphate also seems to occur evenly across the field at least during the first weeks. Later in the season the distribution of total endosulfan in soil becomes uneven, due probably to a combination of factors such as variable runoff losses between furrows, concentration of stubble and microorganisms in certain parts of the field.

#### ***Endosulfan in runoff water***

There was significant pesticide contamination of all irrigated runoff water after the first spray application. The residues found were generally in the range 1-30  $\mu\text{g/L}$  in runoff at the drop-box, depending on the number of days from the previous aerial application. Values declined to about 2  $\mu\text{g/L}$  one month after spraying, corresponding with the decline in on-field soil residue concentration (see Fig. 3). There was evidence suggestive of much higher concentration of residues in runoff water for the first 2 hours of the runoff event, declining to about half this value in later runoff, but this was correlated with the sediment load. It is important to realize that pesticide residues in irrigation runoff from cotton fields are recirculated within the farm boundary. There has been a high degree of compliance with the guideline that runoff water be retained on-farm.

The amounts of endosulfan residues for different levels of measured runoff, calculated from recording hydrograph data, indicate that 0.1-0.4% of the residues on-field are typically washed off for each 0.1 ml. of runoff per irrigation, with up to 10% leaving through the drop-box during an unusually major storm. Most thunderstorms cause much less movement.

The problem of drift onto nearby pasture has been examined. There has been a need to establish the rate of degradation of endosulfan and other pesticides on pasture in order to establish the periods necessary to quarantine pasture onto which a pesticide has drifted.

There is a sound basis, therefore, for the cotton industry's decision prohibiting the feeding of cotton trash to livestock since this program began (as an outcome of the experience with Helix).

The study has shown the importance of the degree soil exposure during pesticide applications in the extent of environmental risk. Thus, high cotton canopy cover can mitigate against high concentrations of pesticide in soil and in runoff. The advent of transgenic Ingard cotton that does not require early applications of endosulfan when soil is highly exposed, is therefore most welcome.

The fate of endosulfan in soil, rapidly forming significant concentrations of equally toxic endosulfan sulphate that persists for several months, means that a cotton field can act as a strong source of pesticide residues in runoff water for several months after applications (see Fig. 3). Even the largest storms only remove a small fraction of the total pesticide bound to soil. Consequently, irrigation and storm runoff must be retained on-farm, as far as possible, by proper management of water including the provision of the maximum water storage. In order to conserve water, there has been good compliance on cotton farms with recommendations to re-circulate tail water. This contains endosulfan and other pesticides on-farm to degrade.

The results of this study focused on endosulfan have already found application in the development of best practices by the cotton industry. In addition, the experience gained in this project has been utilized in pre-registration trials conducted in the last 2-3 years for new chemicals being promoted by chemical companies. The protocols developed for endosulfan provide methods that can often be directly applied to test new chemicals under commercial conditions for cotton production.

### Conclusions

Despite the rapid dissipation of the majority of the endosulfan applied to cotton fields in the first few weeks after application, the remaining residues require careful management to prevent significant off-farm contamination. The results of the project show that in very large storm events, it may be impossible to prevent movement of endosulfan residues off-farm to nearby wetlands and rivers. Since storms occur in most seasons, the possibility of some contamination of rivers from transport of endosulfan in surface waters must be accepted. However, better water management

on farms and other best management practices such as band spraying to reduce the extent of soil contamination, can make significant reductions in the risks to the off-farm environment and to farm produce.

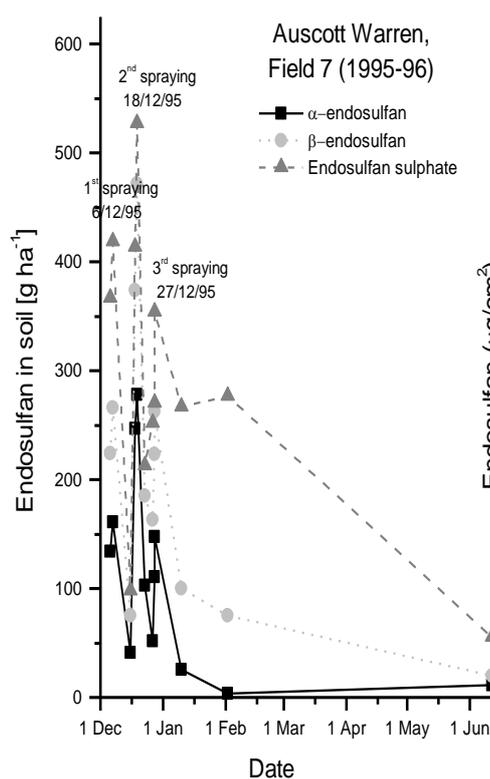
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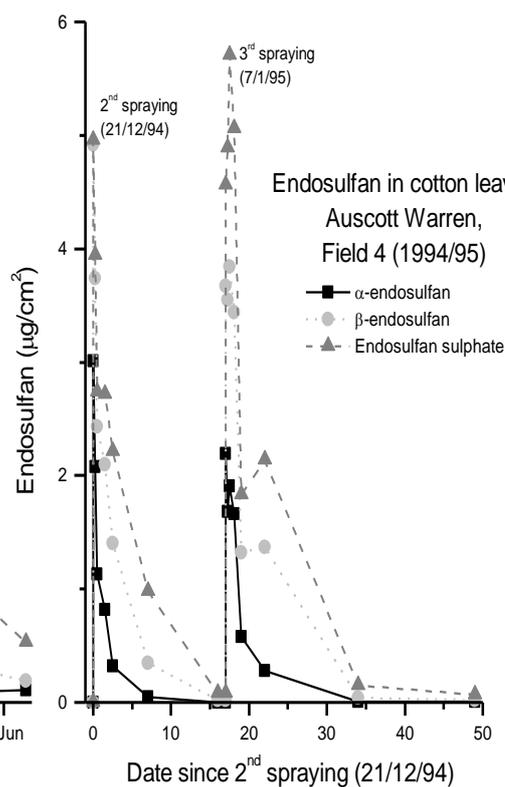
**Table 1. Estimated half-life in days of endosulfan in soil of cotton growing areas.**

| Year    | Field | Phase | a-endosulfan | b-endosulfan | E. sulphate | Total Endosulfan |
|---------|-------|-------|--------------|--------------|-------------|------------------|
| 1993/94 | 21    | 1     | 5.5          | 6.8          | -           | 4                |
|         |       | 2     | 10.5         | 103          | 120         | 180              |
| 1994/95 | 4     | 1     | 1.8          | 4.1          | -           | 2                |
|         |       | 2     | 65           | 86           | 152         | 105              |
| 1995/96 | 20    | 1     | 5.7          | -            | -           | 6                |
|         |       | 2     | 35.7         | 40.2         | 63          | 129              |
| 1995/96 | 7     | 1     | 3.7          | 4            | -           | 5.2              |
|         |       | 2     | 7.8          | 119          | 105         | 137              |
| Average |       | 1     | 4.2±1.8      | 4.9±1.6      | -           | 4.3±1.7          |
|         |       | 2     | 29.7±26.6    | 87±34        | 110±36.9    | 137.7±31.3       |

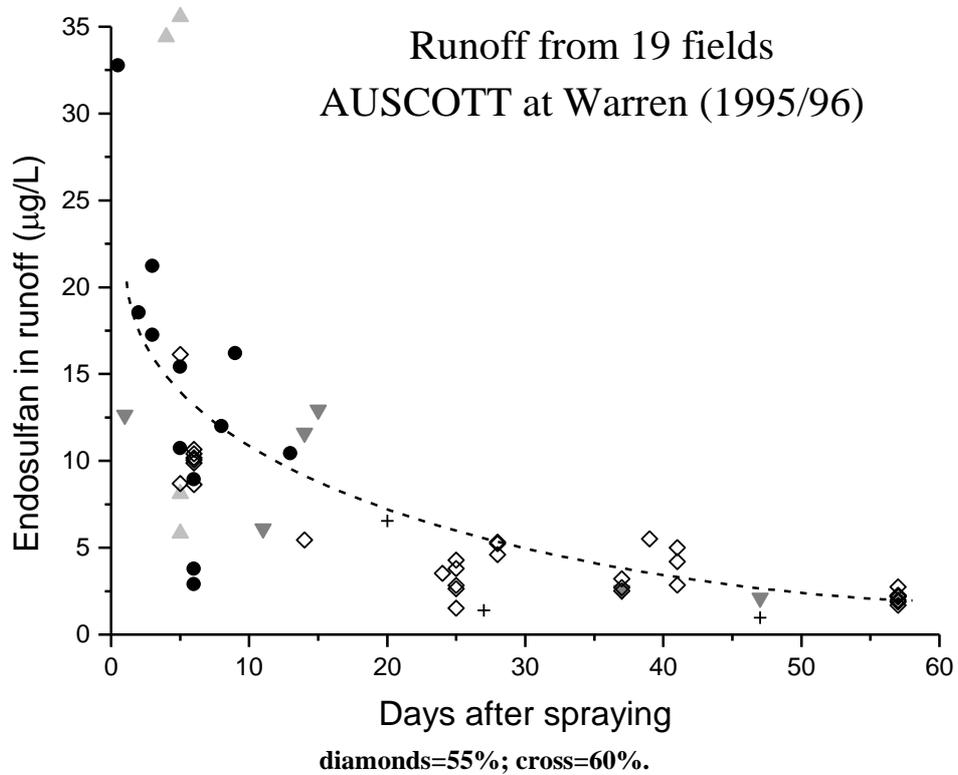
**Figure 1. Typical rate of dissipation of total endosulfan from soil on cotton fields (cumulative data). Endosulfan sulphate, probably mainly formed by fungi in soil, is the most persistent residue.**



**Figure 2. Rapid decline of total endosulfan residues (cumulative data) in cotton foliage. Even endosulfan sulphate, a metabolic product of endosulfan, particularly the  $\alpha$ -isomer, is degraded rapidly.**



**Figure 3. Endosulfan residues in runoff from cotton fields. The decline in residue concentration in irrigation runoff in several return drains is well correlated with the declining concentration in soil (see Figure 1). Different symbols indicate various degrees of field canopy cover at the time of application: circles=20%; squares=30%; triangles=40%;**



**Figure 4. Degradation of endosulfan on pasture. These data (Kennedy *et al.*, 1998b) indicate that a quarantine period of approximately 4 weeks is needed to achieve acceptable residue concentrations in feed for livestock.**

