SPECIAL SUBMISSIONS

Off-Site Movement of Endosulfan from Irrigated Cotton in New South Wales

I. R. Kennedy,* F. Sánchez-Bayo, S. W. Kimber, L. Hugo, and N. Ahmad

ABSTRACT

The fate and transport of endosulfan (6,7,8,9,10,10-hexachloro-1,5, 5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide) applied to cotton (*Gossypium hirsutum* L.) fields were studied throughout three consecutive years on two selected locations in New South Wales (Australia). Rates of dissipation from foliage and soil, volatilization from the field, and transport of residues in irrigation and/or storm runoff waters were measured in order to estimate a total field balance. Dissipation of endosulfan from both foliage and soil is best explained by a two-phase process rather than by a first-order decay. Half-lives of total endosulfan toxic residues (α- and β-endosulfan and the sulfate product) in the first phase were 1.6 d in foliage and 7.1 d in soil, and could be explained by the rapid volatilization of the parent isomers in the first 5 d (up to 70% of endosulfan volatilizes). In the second phase, half-lives were 9.5 d in foliage and 82 d in soil, mostly due to the persistence of the sulfate product. Concentration of endosulfan residues in runoff water varied from 45 to 2.5 μg L^{-1} depending on the residue levels present on field soil at the time of the irrigation or storm events. These in turn are related to the total amounts applied, the cotton canopy cover at application, and the time since last spraying. Most of the endosulfan in runoff was found in the water phase (80%), suggesting it was bound to colloidal matter. Total endosulfan residues in runoff for a whole season accounted for no more than 2% of the pesticide applied on-field.

The cotton industry is one of the largest users of chemicals in Australian agriculture, and this dependence on pesticides has caused serious environmental problems, particularly the contamination of rivers and livestock with herbicide and insecticide residues (Whyte and Conlon, 1990). Aware of its responsibilities, the industry has promoted several programs aimed at reducing the use of chemicals in order to ameliorate their negative effects on the environment. Among several initiatives, a joint program involving the Land and Water Resources Research & Development Corporation (LWRRDC; an Australian federal government body), the Cotton Research Development Corporation (CRDC), and the Murray–Darling Basin Commission (MDBC), commenced in 1993 under the title "Minimising the Impact of Pesticides on the Riverine Environment Using the Cotton Industry as a Model". Program goals were to (i) determine the transport and fate of key pesticides applied to cotton, (ii) assess the effect of pesticides used on the riverine ecosystem, and (iii) provide a sound scientific basis for development of management guidelines for the cotton industry. The data obtained were expected to provide a model of how other chemicals may behave in the cotton environment, for developing practical and economic methods to reduce the transport of pesticides from application sites.

Research teams from several universities, government departments of agriculture, land, and water, and the Commonwealth Scientific and Industrial Research Organization (CSIRO), made a cooperative research effort to measure aerial and surface runoff transport of pesticides, and dissipation of their residues from cotton farms. Sampling procedures for air, water, soil, and sediment for pesticide residue analysis were devised, and a quality assurance study within three laboratories was carried out (Kennedy et al., 1998), while studies on the ecotoxicology (Chapman, 1998) and effect of such pesticides on aquatic organisms were established (Brooks, 1998). As a result, a manual for best management practices in the Australian cotton industry was developed (A. Williams, personal communication, 1997).

As part of the above program, the fate and transport of the insecticide endosulfan was studied in two irrigated cotton farms in New South Wales. The main objective of this project was to determine the relative importance of various transport mechanisms of this pesticide from cotton fields (e.g., volatilization, runoff), for there are only disjointed data in the literature. Measurement of the rate of dissipation of endosulfan through the various transport processes was essential. As a result, a chemical balance for endosulfan inputs and outputs in the cotton system was prepared. Also, the study sought to describe the relationship between pesticide movement off-field and the hydrograph in irrigation and storm events, by measuring pesticide concentrations in runoff water and suspended sediment leaving the field. The possible effectiveness of temporary on-farm storages to quarantine contaminated storm and/or irrigation runoff water as a means of detoxification was also investigated. The data set obtained was subsequently used to develop models for endosulfan transport in runoff (Connolly et al., 2001) and vapor (Raupach et al., 2001), and for farm irrigation management (J. Tuite, personal communication, 1996).

Endosulfan was chosen because it is the most commonly used insecticide (J.W.H. Barret, S.M. Peterson, and G.E. Batley, personal communication, 1991) and

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Abbreviations: GC, gas chromatography.

the main contaminant of the riverine system in areas where cotton is grown (Cooper and Muschal, 1998). At the start of this study the reasons for its widespread contamination in rivers were unknown, though the blame was placed on surface transport from irrigation and storm runoff. Cotton growers were told to recycle the irrigation water and build water storages to contain residues removed from the field by irrigated runoff (tailwaters), but still the storm runoff remained uncontrollable. Contamination of livestock, however, was presumed to be the direct effect of drift onto grazing pastures and required different solutions.

Commercial endosulfan is a mixture of two isomers, alpha (α) and beta (β) endosulfan in a ratio of 7:3, and is usually applied from aircraft as emulsifiable concentrate (EC) or as ultra-low volume formulation in vegetable oil (ULV) to control the cotton bollworm (*Helicoverpa armigera*) and native budworm (*H. punctigera*) in Australian cotton crops. Solubilities in water of 0.32 and 0.33 mg L^{-1} for the respective isomers, and a combined vapor pressure of 9×10^{-3} mm Hg have been reported (Goebel et al., 1982). The formation of endosulfan sulfate in soil is carried out by fungi (Martens, 1977), microorganisms (Miles and Moy, 1979), and collembola (Park, 2000). Archer et al. (1972) observed formation of nontoxic diol, ether, hydroxy-ether, and lactone forms, after exposure of endosulfan to UV radiation. Hydrolysis in water also produces the diol (Peterson and Batley, 1993), and hydrolysis is faster in alkaline media, with half-lives of the mixture being 28, 5.7, and 0.7 d at pH 5, 7, and 9 respectively (Southan and Kennedy, 1995). Endosulfan is particularly toxic to fish (median LD_{50} 3.6 μg L^{-1}), frogs (Berrill et al., 1998), and other aquatic organisms, with the toxicity of α-endosulfan being greater than the β isomer (Goebel et al., 1982). Although the toxicity of the sulfate product to fish is considered to be lesser than that of the parent isomers (Williams and Chow, 1993), the combined residues of α, β, and sulfate must be taken into account in environmental studies of this insecticide.

Although the dissipation of endosulfan from soils of Australian cotton regions was found to be faster than in soils from cold temperate regions of Canada (Stewart and Cairns, 1974), the persistence of the sulfate product in soil (Kimber et al., 1995) warranted a further reconnaissance study on this chemical to ensure its safer use. The present study, therefore, responded to the need the cotton industry had for model scientific data that could be useful in drawing general guidelines for better management.

METHODS

Description of Field Sites

Field studies were carried out for three consecutive years on Auscott farms at Narrabri and Warren, New South Wales (NSW). Since both farms are commercial enterprises that grow cotton in rotation with wheat (*Triticum aestivum* L.), different fields were selected each year according to the availability of cotton crops. Residues of endosulfan in the soil also had to be measured each year to establish a baseline.

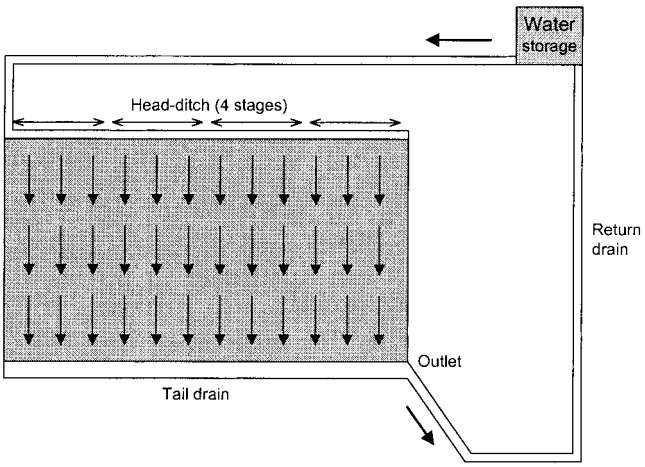

Fig. 1. Diagram of a typical irrigated cotton field showing four irrigation stages and the direction of the water.

The Narrabri farm is located in the middle Namoi valley (30°S) and comprises 3713 ha of cropland on grey cracking clays (Vertosols) with strong self-mulching surfaces (Wright, 1968) overlying alluvial sediments. Surface layers are dark grey or brown color, with 10 to 20 mm subangular blocky structure and 2 to 5 mm granular structure. These soils are very strong, friable, and prone to forming large deep cracks from the surface when drying. A soil survey by CSIRO (McGarry et al., 1989) found the soil pH in the range 8.0 to 8.7, with little organic carbon (0.9%) and 65% clay, 17% silt, and 16% sand. At this farm, Field 21 (82 ha) was selected for the first year (1993–1994 season), mainly on the basis of its crop history, which showed that no endosulfan had been sprayed there for almost two years since 21 Jan. 1992.

The Warren farm is located several hundred kilometers distant in the lower Macquarie Valley (32°S) and comprises 4941 ha of cropland. Most soils at this farm are dark grey to black cracking clays (Vertosol), similar to those of the Namoi valley—60% clay, 25% silt, 13% sand, and 1% organic carbon, with pH in the range 7.7 to 8.6. Coarse red soils are found in certain areas. The latter soils have lower clay content (52%) and more sand (30%), and drained more freely than Vertosols (McKenzie, 1992), but their pH was also measured in the range 7.8 to 8.2. At this farm, Field 4 (57 ha), on grey cracking clay with patches of red soil, was chosen for study in the second year (1994–1995), and Fields 7 (120 ha) and 20 (57 ha) on grey cracking clay in the third year (1995–1996). Farm records showed that neither field was used for growing cotton in the previous season, leaving at least one year without endosulfan application.

Irrigated cotton requires a regular input of water during the summer growing season. At the selected farms, a flood irrigation took place every 3 or 4 wk, thus totalling five or six irrigations per field and season. Water is applied by gravitation from a head ditch into furrows running across the field, and the excess water is collected at the other end (tail drain) and discharged through an outlet into a return drain that takes it to the on-farm storage (Fig. 1). The slope of the fields (1/1500 to 1/1000) ensures the rain runoff also follows the same path whenever a large storm occurs.

Endosulfan Application

Throughout this study, endosulfan was applied from aircraft as an ultra-low volume (ULV) Thiodan formulation at a rate of 3 L ha^{-1} (750 g a.i. ha^{-1}). As the experimental fields did

Table 1. Deposition of endosulfan immediately after being applied to cotton crops.

Date of application	Field no.	Canopy cover	Foliage	Soil	Soil†
		%	— mg kg^{-1} —		% applied
13 Dec. 1993	21	–	3.3	0.33	25.4
6 Jan. 1994	21	–	0.6	0.54	53.9
2 Dec. 1994	4	5‡	–	0.30	19.6
21 Dec. 1994	4	23	51.6	0.71	34.4
7 Jan. 1995	4	55	37.7	0.46	16.3
6 Dec. 1995	7	–	–	0.82	55.9
14 Dec. 1995	20	–	–	1.07	72.8
18 Dec. 1995	7	16	163.8	1.03	57.2
23 Dec. 1995	20	23	134.7	0.88	48.8
28 Dec. 1995	7	–	29.8	0.69	13.6
9 Jan. 1996	20	54	126.2	1.00	44.2

† Excluding residue build-up from previous applications.
‡ On 23 Nov. 1994, prior to the first application of the 1994–1995 season.

not differ in treatment from other fields on-farm in regard to application of chemicals, irrigation, and other agronomic practices, the number and timing of endosulfan applications varied each year (Table 1) in accordance with farming needs. Three applications per season took place on Fields 21, 4, and 7 (total load of 2250 g a.i. ha^{-1}), and four on Field 20 (total load of 3000 g a.i. ha^{-1}).

Sampling Design and Data Collection

First Year, 1993–1994

Endosulfan residues in soil were first characterized in regard to their distribution in soil profiles and spatial patterns across the sprayed field, while dissipation in time was also estimated. To detect spatial–temporal variability in endosulfan residues on-field, a stratified design of 90 regular blocks on Field 21 (Narrabri) was chosen, with sampling of both soil and foliage in 24 selected blocks. Within a block, a variable number of soil samples (3 to 15) were taken at 1, 2, 3, 24, 34, 73, 121, 245, and 352 d after the second endosulfan application (13 December). Each soil sample was a composite of 20 cores (4.5-cm diam.) from the surface layer (5 cm), which were thoroughly crushed and mixed with a spatula on a glass tray. A subsample of this mixture was placed in a clean brand-new 250-mL glass jar. To investigate the effect of furrow aspect on spatial distribution of pesticide residues, samples were taken separately from the top, slope, and bottom of the furrows. Sets of four soil samples from the field, taildrain, and return drain were taken at 2-cm intervals of depth to 10 cm on Days 25, 69, and 245 to measure residue loads deposited off-field after irrigation events.

To estimate the endosulfan dissipation rates from cotton foliage, 1-L glass jars were filled with leaves collected at random from several plants in each of the 24 blocks. Sampling was done on Days 0, 1, and 5 after the second application, and Days 2 and 10 after the third application.

All sample jars were sealed with aluminum foil liner fitted to a new plastic crew cap (Australian Standard 2031.1; Standards Association of Australia), and cooled in an insulated ice box for transportation to a freezer, where they were kept at subzero temperatures (−20°C) until the time of analysis.

Second Year, 1994–1995

Similarly, in the second year another stratified design of 18 blocks on Field 4 was chosen for soil and plant sampling, but this time sampling was performed in all blocks. In order to estimate more accurate dissipation rates from both soil and cotton plants, a more intensive sampling was done at 3 h, 6 h, 1 d, 2 d, 6 d, and 17 d after each endosulfan application, plus at 30, 150, and 205 d after the last application. Each soil sample was a composite of six cores taken on a logarithmic basis along a transect, as results from the previous year showed that no significant differences in the mean and variance of residues could be obtained using this number of cores. The same sampling technique as the previous year was used. Sediment samples from the tail drain were also taken on six occasions immediately after each irrigation event throughout the season to check residues deposited off-field.

To estimate the amounts of pesticide falling on both soil and canopy immediately after spraying, filter papers strips (57 × 2.5 cm) placed on wooden slats on the ground and on plates 1 m above the canopy (20 × 45 cm) were placed at 10 locations. Paper strips were collected immediately after application of endosulfan, placed in brand-new 250-mL glass jars, and transported and stored as the soil and plant samples. For the 21 December and 7 January applications, integrated studies on drift (Woods et al., 2001) and volatilization (Edge et al., 1998) were carried out. For the latter study, two air samplers were set up 100 and 200 m into the field, with the air intake positioned 1 m above the crop. The air was passed at 4 L min^{-1} through carbon cartridges fitted with a fibre glass filter to remove dust. The cartridges were removed at 4-h intervals for the first 24 h and then at 12-h intervals for the next 4 d.

To determine the distribution of insecticide residues in plants, separate samples from outer and inner leaves, bolls and/or flowers, and stems were taken. The entire foliage from nine whole plants was collected on each sampling time, to allow estimation of endosulfan loads per plant. Since the amount of pesticide adsorbed by plants was expected to depend largely on their exposed surface at the time of application, which increases as the plant develops, an estimate of the plant canopy was made prior to each application and twice more throughout the growing season. Plant cover was calculated as the percentage of horizontal shadow cast by cotton plants, measured on a meter stick with 1-cm markings placed along and across 10 random beds within each field. Plant height was also recorded, and a relationship between both parameters was established.

A few days before the crop was defoliated, two sets of 10 cotton plants were taken to a nearby ground-level site where they could experience natural decay conditions. Sampling of dried and/or decayed leaves, stems, and bolls in the subsequent months was done on three occasions at 151, 206, and 282 d after application, so as to obtain information on the persistence of the insecticides in this kind of trash under field conditions. Lint and gin trash were also analyzed for endosulfan residues.

A comprehensive hydrological study was also conducted, with intensive monitoring of flows during the hydrograph using two flumes distant 10 m apart installed on furrows about 50 m into the field, and by a stage height indicator installed at the outlet of the field. Total runoff discharge was also measured in the return drain using automatic equipment recording on data loggers, installed by the NSW Department of Land and Water Conservation. The objective was to estimate the pesticide loads carried off-field by runoff water in the course of the season. During four irrigations and three storm events, runoff water samples (i.e., water and suspended sediment) for pesticide and sediment analysis were taken at each flume and field outlet. Manual sampling using 1-L amber glass bottles was performed at regular intervals of 1 h, with 5 to 12 samples collected each time according to the duration of the events. Bottles were sealed with Teflon-lined screw caps, and cooled in an insulated ice box for transportation to a fridge, where they were kept at 4°C until the time of analysis.

Third Year, 1995–1996

In the final year of the study, the main focus was on transport processes associated with irrigation practices rather than on dissipation of pesticide residues from field. To this effect, regular soil sampling from 19 fields and their corresponding irrigation outlets throughout six irrigation periods was carried out, with two soil samples taken from the field and two runoff water samples collected from the outlets each time. A detailed study of pesticide and sediment loads along two furrows distant 20 m apart in Field 20 was also carried out during two irrigations (20 Dec. 1995 and 17 Feb. 1996). Paired runoff samples were taken at 1/4, 1/2, and 3/4 of each furrow length plus at the tail drain. Two minor storms were recorded in the third year, but runoff samples were taken from the only one that produced some discharge. Total runoff discharge from Field 20 was also measured at the field outlet using automatic equipment recording on data loggers, installed by the NSW Department of Land and Water Conservation.

An associated degradation study in ponded runoff from irrigation water discharged into an excavation from Field 20 on 20 December was set up to determine the effective remediation of this system in reducing endosulfan residues transported in runoff. The water was sampled at 0, 1, 2, 3, 6, 7, 9, 11, and 15 d after being stored in the pond. Sediment cores from the bottom of the pond were taken at 2, 3, 6, 7, 11, 15, and 24 d to monitor the sedimentation of residues. The depth of the water column was measured at 0, 4, 13, and 24 d in order to calculate a mass balance of endosulfan residues.

To estimate the residue loads on Fields 20 and 7 and their dissipation throughout the season, random sampling of four soil samples (10 cores composite per sample) and four cotton foliage samples (all plants within 1 m bed) per field and date was carried out at 0, 1, 4, 8, and 16 d after each endosulfan application, plus at 30, 65, and 154 d after the last application. Plant cover was determined for each of these fields before endosulfan sprayings as in the previous year.

Analysis and Quality Assurance

A total of 782 soil, 58 sediment, 20 paper strip, 341 foliage, 27 trash and/or litter, and 671 water samples were analyzed using solvent extraction and gas chromatography (GC) at the Biological and Chemical Research Institute laboratories, NSW Agriculture at Rydalmere.

The analytical method has been described elsewhere (Ahmad et al., 1999). Extraction of soil was done by shaking the sample with a solvent mixture of nanograde dichloromethane and acetone (80:20 v/v). Moisture content in soil samples was determined during the analytical process, using dry weight obtained on exposed subsamples dried overnight at 105°C. Soxhlet extraction of foliage was achieved with 25 g of fresh leaves placed in a thimble and extracted with 300 mL of dichloromethane–methanol (80:20 v/v), including washings. The sample was refluxed for 4 h, with sufficient heat to cause refluxing about five times an hour. For the water samples, a 500-mL aliquot was added to a separating funnel and mixed with 30 mL of dichloromethane. The mixture was shaken for 2 min with frequent venting at the stopcock. The coextractives from soil, foliage, and water samples were removed from the extract on an alumina column, and then concentrated in a Kuderna–Danish assembly, exchanging the solvent with *n*-hexane. Carbon cartridges from air samplers were extracted with a mixture of toluene and hexane (80:20 v/v), followed by sonication (Ultrasonic Pty. Ltd., Sydney, Australia) for 30 min, and then 5 mL of the solvent were diluted to 25 mL with nanograde hexane. The eluates (1 μL) were analyzed with a Varian (Walnut Creek, CA) 3400 GC with dual ECD detectors using a split sample chromatographed on DB-5 and DB-17 capillary columns (30 m × 0.3 mm; 0.25-μm liquid phase film). Dibutyl chlorendate (1.08 μg) was added as a surrogate standard. Recoveries of 86.8 ± 13.3% for total endosulfan residues (α, β, and sulfate product) were obtained.

A larger number of soil and water samples were analyzed using CSIRO immunoassays (ELISA) for total toxic endosulfan residues (Lee et al., 1995) at the University of Sydney and at the Trangie Research Centre, NSW Agriculture, as part of a Co-operative Research Centre for Sustainable Cotton Production project to validate immunoassay for field studies. Good agreement between results obtained by GC and ELISA for soil was obtained ($r^2 = 0.89$), but at least 10 g of well-mixed soil is required for extraction (Lee et al., 1997). However, the endosulfan immunoassay often gives greater values for residues in runoff samples than analysis by GC: this may indicate real differences, since immunoassays are conducted soon after being collected, before inevitable losses occur by rapid volatilization of pesticides such as endosulfan, or by hydrolysis during transportation to the analytical laboratory. It was also found preferable to freeze water samples for immunoassay, or to add acetate buffer (pH 5.5), if analysis could not be conducted immediately.

A parallel quality assurance program on the analytical work by three independent laboratories gave confidence in the accuracy of the results of the three-year study, as reported elsewhere (Kennedy et al., 1998).

Data Processing

Soil residue data from the sampling blocks in the stratified design of the first two years were compared by analysis of variance throughout the study period, in order to detect any variability on endosulfan concentrations on-field. Regressions fitted to the transformed logarithmic data were used to determine half-lives in soil and foliage following each application, and in water runoff collected after each irrigation and storm event. A paired *t*-test was used to compare the residue concentrations and sediment loads in the two sets of water runoff samples collected along the furrows in Field 20.

Residue concentrations in soil (mg kg^{-1}) were converted to loadings per field area in g ha^{-1}, and residues in plant samples expressed on a surface area basis (μg cm^{-2}) were also converted to mg kg^{-1}. From the residue loadings in runoff samples and the total water discharged on each occasion, it was possible to estimate the total amount of endosulfan leaving the field in one season. Together with the volatilization measurements in the second year, these data were used to estimate a chemical balance for the entire Field 4 on the second year of this study.

RESULTS

Deposition of Insecticides on Soil and Cotton Plants

Measurements of plant canopy cover throughout the seasons 1994–1995 and 1995–1996 indicate that plant cover varied from 5% at the time of the first endosulfan application (early December) to 54% by the end of the endosulfan spraying period in mid-January (Table 1) and up to 90% later in the season. This indicates a great variation in soil exposure to the pesticides applied. Thus, the majority of insecticide is expected to fall on the soil in the early applications, while in the later sprayings up

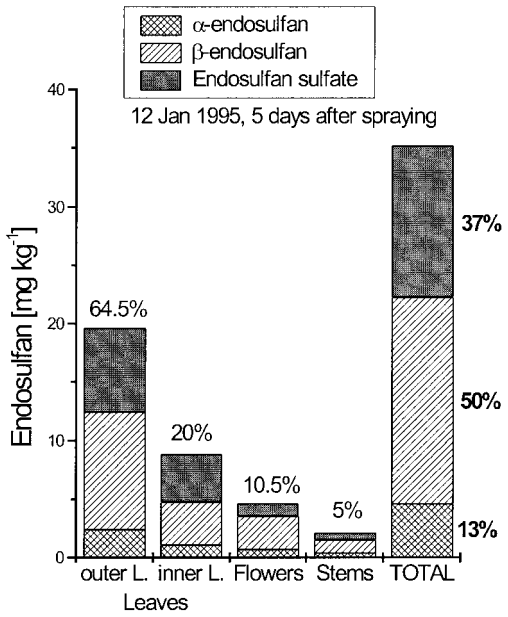

Fig. 2. Distribution of endosulfan residues in cotton plants. The majority of residues are found in the leaves.

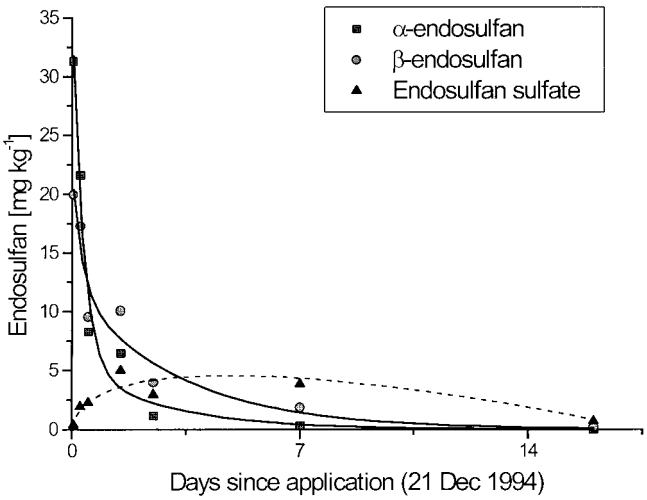

Fig. 3. Typical dissipation of endosulfan in cotton leaves from Field 4 at Auscott Warren. Formation of the sulfate product is less than 10% of the initial amount.

to half of the endosulfan applied would fall on the plants. Deposition on soil seems to depend on the canopy cover, but the data obtained in this study for different fields and seasons are not well correlated ($R^2 = 0.42$) to the plant canopy cover at the time of application, with deposition on plants being even more variable. This may reflect the differences in meteorological conditions at application, particularly wind speed and humidity (Craig et al., 1998).

Residues in Plants

Distribution of Residues in Cotton Plants

Data from a late application of endosulfan (1 July 1995) on Field 4 show that most of the insecticide adsorbed by cotton plants is found in the outer leaves (65%), with the inner leaves and flowers contributing significantly (30%) to the total uptake, whereas only a small proportion (5% or less) was found in the stems (Fig. 2). Thus, residues in leaves account for about 80% of the total amount in cotton plants, and estimates of the total load of pesticides for the entire field crop can be made.

Dissipation of Residues from Plants

Initial concentrations of α- and β-endosulfan in foliage varied markedly among applications, from 29 ± 11 mg kg^{-1} measured to 164 ± 83 mg kg^{-1}, the variance probably due to environmental factors such as temperature, humidity, and wind acting upon the crop structure of each field. The concentrations of both endosulfan isomers declined extremely rapidly in the first 2 to 3 d and the rate of dissipation then slowed down. Endosulfan sulfate was detected almost immediately after application, its concentration increasing rapidly in the first week and reaching up to 10% of the initial residues in foliage, and then decreasing steadily over an extended period (Fig. 3).

Concurrent measurements on volatilized endosulfan above the crop on Field 4 showed that the rapid decline in endosulfan concentration in the first 5 d is due to volatilization, which may account for 64% (1 July 1995) to 90% (21 Dec. 1994) of the total dissipation in that period. After this time, volatilization is minimal as total endosulfan in air reaches a plateau (Fig. 4).

This pattern of dissipation of endosulfan parent isomers in cotton foliage is better described by a second-order kinetic curve than by a first-order curve, and this applies equally to the total endosulfan residues (Fig. 5). In the first phase, up to 4 to 5 d, average half-lives of 0.9 d for α- and 2 d for β-endosulfan were estimated, and most of this dissipation is related to the rapid volatilization observed while at the same time a significant amount (9 ± 11%) of endosulfan sulfate is formed. For total endosulfan residues, the half-life in this first phase is 1.6 ± 0.7 d.

In the build-up phase, from Day 4 or 5 onward, dissipation of the two parent isomers and the sulfate product follow the typical first order decay with estimated half-lives of 13 d for α-endosulfan, 8 d for β-endosulfan, and 7.6 d for endosulfan sulfate (Table 2). However, residues of α-endosulfan of 0.04 mg kg^{-1} were found after 83 d in plants from Field 20, giving an estimated half-life of 42 d for this isomer on that field. Overall, the average half-life for total endosulfan residues in cotton foliage in the second phase was estimated as 9.5 ± 8.2 d.

Persistence in Litter and Trash

Concentrations of endosulfan in foliage and stalk trash collected from Field 4 did not show a clear decay pattern from the time of defoliation (mid-April 1995) until six months later (19 Oct. 1995). Although residues in foliage litter fell from 1.22 mg kg^{-1} of dried matter to 0.34 mg kg^{-1} during this time, there was an increase from 0.06 to 0.14 mg kg^{-1} in stalks, which could be the result of contamination from underlying soil or blown

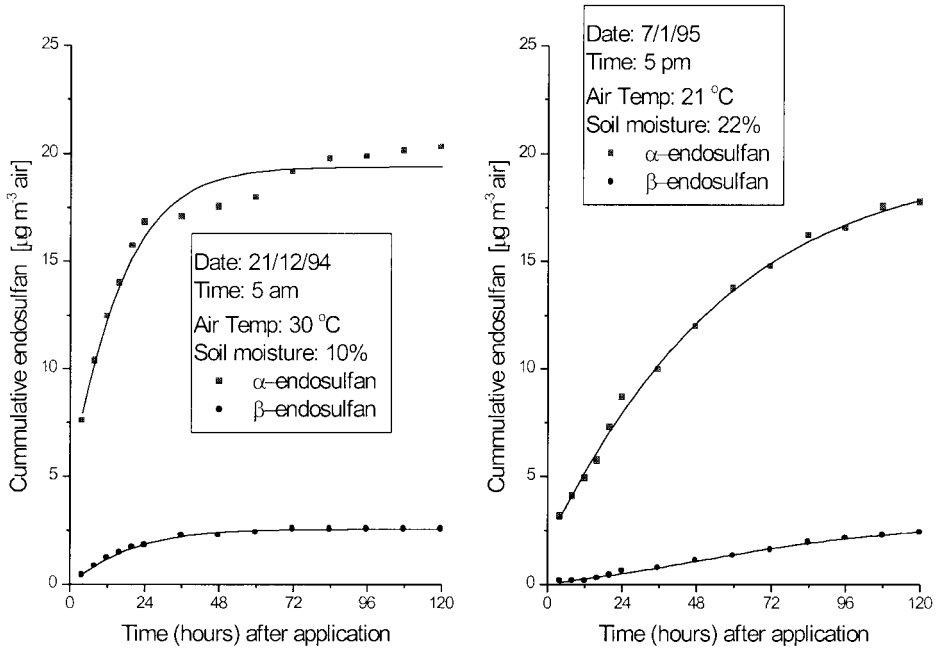

Fig. 4. Volatilization of endosulfan parent isomers under two different field conditions. Hot conditions following the early application on 21 Dec. 1994 resulted in 90% of the endosulfan residues disappearing after 5 d, whereas on the late application only 64% of residues disappeared in the same period.

dust from nearby fields. An estimate of half-life for total endosulfan in the overall exposed plant material is 65 d. Gin trash had similar residue levels to those found in the field (Table 3), while no endosulfan could be detected in lint or in cotton seed.

Residues in Soil

Distribution of Residues in the Soil Profile

About 90% of endosulfan residues were present in the top surface layer (0–6 cm) of Field 21, their concentration declining sharply with depth and being negligible (<2%) beyond 8 to 10 cm (Fig. 6). Samples from the field, tail drains, and return drain showed the same pattern of distribution, but endosulfan concentrations in the return drain were significantly lower than those from the field and tail drains. These results are consistent with previous studies on this chemical (Kimber et al., 1995).

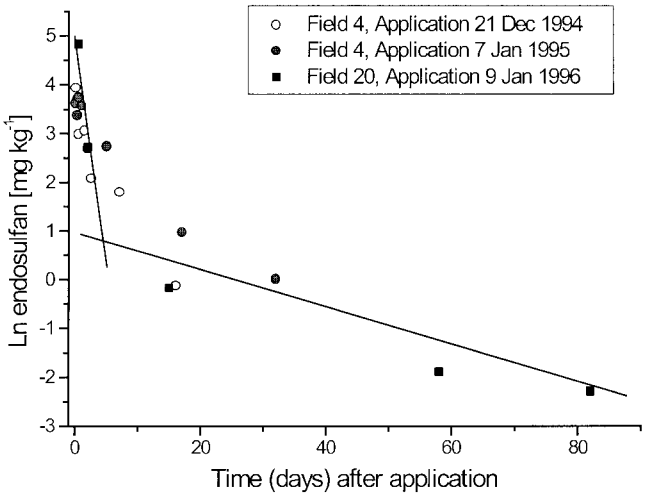

Fig. 5. Second-order dissipation of total endosulfan residues in cotton foliage.

Spatial Variation of Field Residues

Statistical analyses (analysis of variance [ANOVA]) of the data for the stratified design by rows and columns on Fields 21 and 4 indicate that in the first three months there was no significant difference in concentrations of endosulfan residues among strata, which implies that aerial applications provide an even spread of pesticide on the cotton field (Table 4). However, later in the year the distribution of total endosulfan in soil became more uneven, due probably to a combination of factors such as variable water runoff losses across furrows, the influence of crop stubble, microbial degradation in certain parts of the field, and other factors.

Endosulfan concentrations in cores taken from the bottom of furrows at Field 21 were invariably lower than in those from the tops of beds in the first 3 d after application, and this difference was significant ($P < 0.05$), but disappeared within 2 d. No convincing explanation could be found to explain this difference other than a greater soil compaction in the case of the bottom samples as a result of tractor traffic, or dripping of excess endosulfan from the plants to the top beds.

Dissipation and Degradation of Endosulfan Residues in Soil

All fields studied had some low levels of residual endosulfan in soil at the beginning of each cotton season, in the range 0.01 to 0.08 mg kg^{-1} (60 g ha^{-1}), mostly in

Table 2. Half-life of endosulfan in foliage of cotton plants. Goodness of fit (r^2) is shown only for total residues.

Date of application	Field	Half-life							
		α–endosulfan		β–endosulfan		Endosulfan sulfate	Total endosulfan		
		Phase 1	Phase 2	Phase 1	Phase 2	Phase 2	Phase 1	Phase 2	r^2
		days							
13 Dec. 1993	21	0.7	–	1.3	–	–	1.2	–	0.86
21 Dec. 1994	4	0.6	2.8	1.2	2.9	5.5	1.1	4.0	0.84, 0.95
7 Jan. 1995	4	1.1	4.9	2.0	5.4	8.6	1.6	7.2	0.66, 0.96
18 Dec. 1995	7	1.1	–	2.7	–	–	2.2	–	0.76
23 Dec. 1995	20	1.0	1.8	3.0	2.5	3.1	1.6	5.2	0.94, 0.88
28 Dec. 1995	7	1.2	–	2.1	–	–	2.7	–	0.98
9 Jan. 1996	20	–	42.3†	–	21.0	13.3	–	21.6	0.96
Average		0.9 ± 0.3	13.0 ± 19.6	2.0 ± 0.8	8.0 ± 8.8	7.6 ± 4.4	1.6 ± 0.7	9.5 ± 8.2	

† Residues up to 83 d; see also Fig. 4.

the sulfate form. Consecutive applications of endosulfan to these cotton crops raised the total residue concentration in soil to a maximum level of 1.07 mg kg^{-1} (546 g ha^{-1}) on Field 20. Data from 19 fields indicate that the highest residues of endosulfan observed in soil—reaching almost 2 mg kg^{-1}—occurred always after the second or third applications as a result of build-up when fields with little plant canopy are sprayed. Subsequent applications do not increase these residues any further because plant cover increases markedly later in the season, thus offsetting deposition of pesticide on soil.

Following a similar pattern as in foliage, dissipation of endosulfan in soil is best described by a second-order kinetic curve where its fast disappearance in the first week after application is correlated with the loss of both parent isomers by volatilization, the extent of which is dependent upon environmental conditions such as temperature, wind, and soil moisture (Southan and Kennedy, 1996). The half-life of total endosulfan in soil in the first phase, 7.1 ± 3.0 d, is about five times longer than that in foliage, but this varied from field to field as the soil and environmental conditions were different for each location, year, and time of application (Table 5).

While α-endosulfan in the first phase has a 3.2 ± 1.5 d half-life in soil, it increases to an average of 69 d in the second phase, in contrast with the 46 d estimated for β-endosulfan. It is known that most of the endosulfan volatilized in the first 5 d is α-isomer (Edge et al., 1998; see Fig. 4), thus explaining its fast dissipation in the first phase. In the second phase, however, a slower rate of overall dissipation seems to reflect the formation in soil of the more stable product endosulfan sulfate, which accounts for 60 to 70% of the residues in soil (Fig. 7). The highest peaks of endosulfan sulfate occurred at variable time after the last application, and usually after a month it represented 9 to 22% of the total endosulfan applied, except in Field 4 where it accounted no more than 4% of the total endosulfan applied. Dissipation of endosulfan sulfate in soil is about 12 times slower than in foliage, with average half-lives of 92 ± 47 d.

Studies on Runoff Water

Irrigation Patterns and Hydrograph

Hydrographs of irrigation runoff were examined for endosulfan residues and sediment loads at Fields 4 and 20. These hydrographs were complex, with repeated and successive flow peaks at the outlets reflecting the irrigation of sections of the fields in several stages, as the sets of siphons were moved along the head ditch. For this reason, it was considered that sampling data for any of these stages would be representative of the conditions occurring through the whole field. Storm runoff, in contrast, usually produced only one flow peak at the tail-drain outlets.

Partitioning of Endosulfan in Runoff Water and Suspended Sediment

Results from the third irrigation on Field 4 were suggestive of a good correlation between endosulfan residues and sediment loads in runoff water, both at the flumes (R^2 = 0.78) set up on-field and at the outlets (R^2 = 0.85) draining the field. This could be a proof that endosulfan in runoff was bound to the sediment component, despite the fact that this correlation was not always obvious in samples taken during other irrigations (in best case, R^2 = 0.5). To clarify this question, analyses of runoff water samples from Field 20 the following year were performed separately on both the aqueous and the suspended sediment fraction, which was obtained by filtration through Whatman glass papers with 0.7-μm pores.

About 80% of the endosulfan load was found in the water and the remainder on suspended particulate and sediment that could be filtered (Table 6). Although endosulfan is not very soluble in water (0.32 mg L^{-1}), a large amount is expected to be in a volume of water 250 times greater than the average suspended sediment found in runoff samples (4 g L^{-1}). However, a partitioning coefficient of 57 100 (Goebel et al., 1982) implies that very likely most of the residues found in the filtered

Table 3. Endosulfan residues in field litter and gin trash, lint, and seed 6 mo after defoliation.

Material	α–endosulfan	β–endosulfan	Endosulfan sulfate	Total endosulfan
	mg kg^{-1} dry matter			
Foliage litter	<0.01	0.27	0.07	0.34
Stalk litter	0.02	0.05	0.08	0.14
Gin trash	<0.01	0.08	0.15	0.23
Lint	<0.01	<0.01	<0.01	<0.01
Seed	<0.01	<0.01	<0.01	<0.01

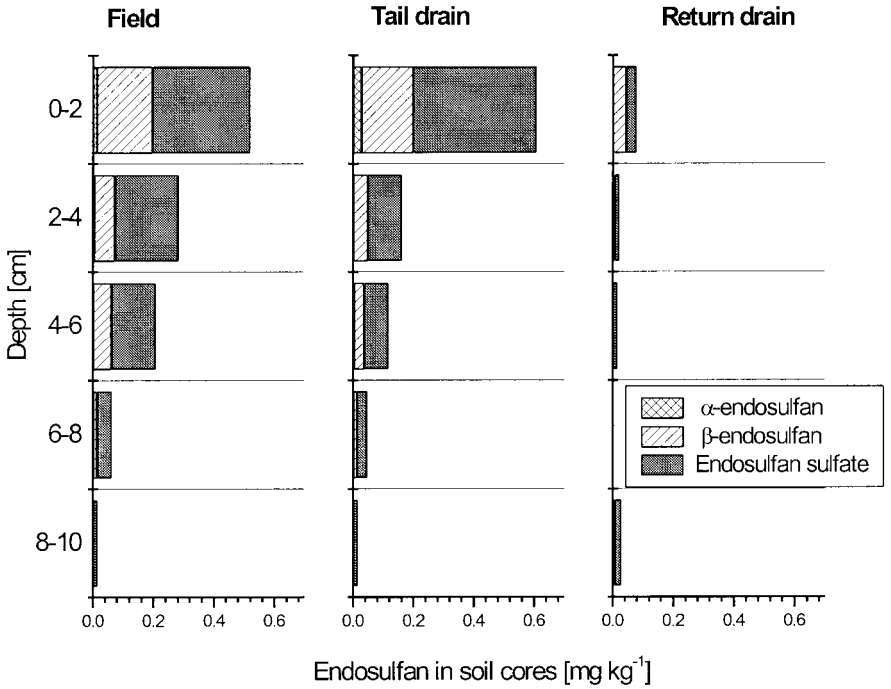

Fig. 6. Endosulfan residues in soil profile (field) and sediment cores from tail and return drains. About 90% of the residues are found in the top 6 cm.

water were in colloidal particles that passed through the filter and not in solution as such.

Endosulfan Residues in Runoff Samples

Analyses of runoff samples taken during irrigation and storm events at the outlet of Field 4 show a significant pesticide contamination of all runoff water throughout the entire cotton-growing season. Highest residue levels were recorded in the early irrigations, about 5 to 10 $\mu g\ L^{-1}$ seven days after the previous aerial application, then declining to about 2 $\mu g\ L^{-1}$ one month after spraying. Also on early irrigations, a much higher concentration of endosulfan was found in runoff collected in the first 2 h of the event, its level declining to about half this value in later runoff, but this difference was not so obvious in late irrigations (Fig. 8).

The drop in endosulfan levels found in runoff samples from late irrigations corresponds with the decline in on-field soil residues, which also fell by half (0.67 to 0.27 mg kg^{-1}), suggesting that the amounts of pesticide removed from the field by irrigation or storm runoff are dependent on the amount of residues present in the soil at the start of a given event. Runoff samples collected during a big storm event on 19 Jan. 1995 (181.2 mm, a 1:50 year event), however, show that residue levels increased with time perhaps as a result of intense water-sheet erosion of the field surface. Further studies on Field 20 confirmed that endosulfan residues in the front

Table 4. Endosulfan residues in soil of Field 4 (Auscott Warren). For each sampling day, no significant spatial variation was observed between rows or columns of the stratified block design (two-factor analysis of variance [ANOVA] analysis).

Date of application	Days after application	Number of samples	Endosulfan	sd	Rows *P* value	Columns *P* value
			mg kg^{-1}			
2 Dec. 1994	2	9	0.32	0.13	0.813	0.534
	6	18	0.34	0.15	0.533	0.206
	9	9	0.28	0.08	0.388	0.271
21 Dec. 1994	0.08	6	0.76	0.11	0.707	0.125
	0.25	7	0.80	0.21	0.642	0.424
	1	7	0.86	0.28	0.682	0.244
	2	7	0.40	0.14	0.989	0.917
	6	19	0.32	0.09	0.524	0.234
	16	12	0.26	0.09	0.778	0.167
7 Jan. 1995	0.08	12	0.68	0.16	0.281	0.094
	0.25	12	0.62	0.23	0.557	0.140
	0.6	12	0.56	0.30	0.215	0.499
	1	12	0.52	0.22	0.681	0.685
	2	9	0.41	0.12	0.596	0.839
	5	7	0.35	0.16	0.322	0.341
	17	24	0.27	0.19	0.976	0.579
	31	15	0.34	0.08	0.468	0.030†

† $P < 0.05$.

Table 5. Half-life of endosulfan in soil. Phase 1 corresponds to Days 1 to 7 after application; Phase 2 from Day 7 onward is only applicable to the last application. Goodness of fit (r^2) is shown only for total residues.

Date of application	Field	Half-life							
		α–endosulfan		β–endosulfan		Endosulfan sulfate	Total endosulfan		
		Phase 1	Phase 2	Phase 1	Phase 2	Phase 2	Phase 1	Phase 2	r^2
		days							
3 Jan. 1994†	21	–	49.9	–	27.2	144.4	–	113.6	0.61
6 Dec. 1995	7	5.2	–	6.3	–	–	4.7	–	0.98
21 Dec. 1994	4	3.6	–	19.0	–	–	11.1	–	0.82
7 Jan. 1995†	4	0.7	58.2	17.1	77.0	117.5	5.8	110.0	0.81, 0.96
14 Dec. 1995	20	3.3	–	5.6	–	–	3.2	–	0.71
18 Dec. 1995	7	3.5	–	13.8	–	–	8.2	–	0.63
23 Dec. 1995	20	4.2	–	8.0	–	–	10.6	–	0.80
28 Dec. 1995†	7	1.6	81.5	4.7	41.7	54.2	6.2	54.6	0.88, 0.77
9 Jan. 1996†	20	–	85.6	–	38.9	50.6	–	51.3	0.89
Average		3.2 ± 1.5	69 ± 17	10.6 ± 5.9	46 ± 21	92 ± 47	7.1 ± 3.0	82 ± 34	

† Last application for each season.

runoff (45.3 ± 6.6 μg L^{-1}) along the furrows were significantly higher ($P < 0.001$) than in the rear runoff (11.7 ± 3.3 μg L^{-1}) at least in the second irrigation of that season, whereas no difference was found in the fifth irrigation. Also, runoff samples collected along a cross-section of the irrigated field showed no consistent evidence of a building up in endosulfan residues while the water moved from the head to the tail of the furrow, though the rear waters from the second irrigation appeared to show that trend.

Runoff samples taken at the outlet of Field 20 showed significantly ($P < 0.001$) higher endosulfan loads than the samples taken at the flumes and/or furrows, while the opposite was found during the first irrigation on this field. The same pattern was also observed the year before at Field 4. Endosulfan loads in runoff at the outlets of 19 different fields, collected during the 1995–1996 season, averaged 8 ± 1 μg L^{-1} (range 1–35), almost twice as high as those in the return drains (4.5 ± 1 μg L^{-1}, range 0.2–15). Highest values were consistently found when the irrigation occurred soon after aerial sprayings. Water from the supply channels around the Warren farm showed concentrations of endosulfan in the range 0 to 7 μg L^{-1}, with highest values of 13 μg L^{-1} in the first week after endosulfan application, suggesting some contamination from aerial sprayings.

Transport of Residues Off-Field

Preliminary results from Field 4 provided a simple regression equation ($y = 7.64 - 0.25x + 0.002x^2$, $R^2 = 0.89$) for calculating endosulfan residues in runoff water (y) with time since application (x). However, endosulfan loads in runoff from outlets of 19 fields at Warren during 1995–1996 season showed greater variation than predicted by this equation, particularly if irrigations took place soon after an endosulfan application (Fig. 9). It appears that the decline in endosulfan concentrations in irrigation runoff is correlated with the declining residues in soil, which to a great extent are determined by the crop canopy cover at the time of application. This variability was reduced when the plant cover and time between consecutive sprayings were taken into account, implying that a multiple regression analysis that includes these parameters is needed to estimate more accurately pesticide residues in runoff water.

Estimates of the total transport of endosulfan off-field by irrigation and storm runoff water are given in Table 7. Total endosulfan residues that left the field at the end of the season accounted for no more than 2% of the total endosulfan applied on Field 4 and 1.5% of that applied on Field 20. However, half the residues from Field 4 were taken by a major storm runoff (Storm 2), while the first irrigation at Field 20 is responsible for most of the residues from this field found in runoff, a result consistent with two endosulfan applications put

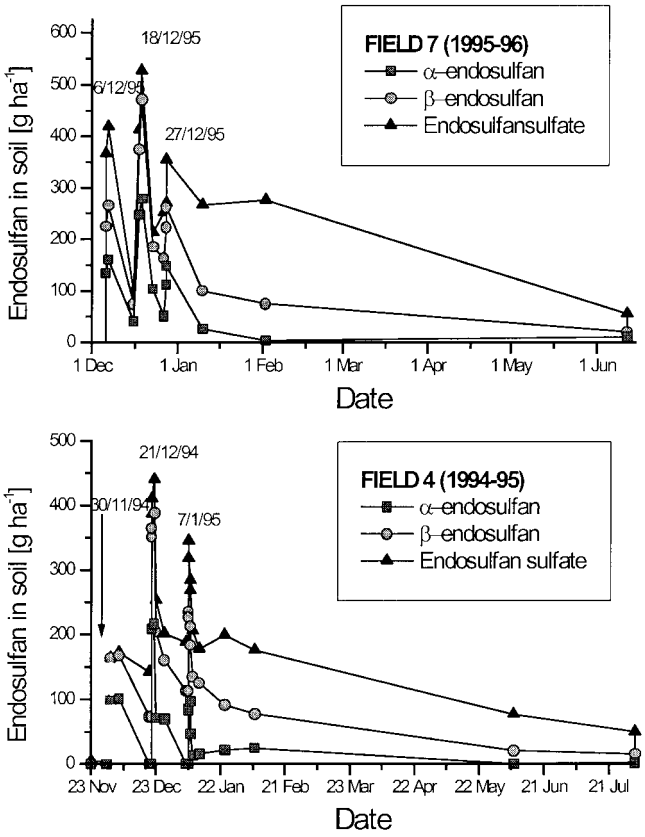

Fig. 7. Dissipation of endosulfan (cummulative data) from soil on two cotton fields at Auscott Warren. Dates of endosulfan applications are indicated. See also Figure 4.

Table 6. Distribution of endosulfan in runoff water and suspended sediment.

	Water fraction		Sediment fraction			
	Furrow	Outlet	Furrow	Outlet	Water	Sediment
	μg L^{-1}				%	
Irrigation 2	28.2 ± 10.1	22.3 ± 7.5	4.8 ± 0.7	1.8 ± 0.5	88.3	11.7
Storm 1	1.7 ± 0.2	2.5 ± 0.4	0.5 ± 0.1	0.4 ± 0.1	81.5	18.5
Irrigation 3	4.5 ± 1.1	8.7 ± 0.2	0.1 ± 0.02	2.1 ± 0.9	85.8	14.2
Irrigation 5	2.1 ± 0.02	3 ± 0.1	0.8 ± 0.2	1.8 ± 0.7	65.1	34.9
Irrigation 6	1.1 ± 0.1	1.9 ± 0.1	0.3 ± 0.04	0.2 ± 0.03	85.5	14.5
Average					81.2	18.8

on very early in the season (30 November and 12 December) when plant canopy cover was less than 10%.

These data show that the major storm event at Field 4 in 1995, which began 11 d after the last aerial application, resulted in 10% of endosulfan residues present in soil at that time being transported off-field in about 130 ML of runoff. This amounted to half of the total endosulfan removed by runoff in the whole season, equivalent to the same amount transported in all six irrigations. Two other local thunderstorms that were monitored in 1995 and one in 1996 were minute by comparison, involving less than 1/1000 of the endosulfan residues being transported off-field.

Dissipation of Endosulfan Residues from a Pond

Runoff water from Field 20 was stored in a pond built nearby. The ponded water initially contained about 200 mg of endosulfan. Three weeks later, the amount of endosulfan in the water column had decreased to about 60 mg. Once again, dissipation of total endosulfan followed a two-stage process, each phase fitting a first-order kinetics with half-lives of 1.5 and 7.8 d. A rapid initial dissipation corresponded with the disappearance of α- and β-endosulfan (Fig. 10a), while the second slower phase of the dissipation was characterized by the presence of the product endosulfan sulfate remaining in the runoff. Total endosulfan on colloidal and suspended sediment (>0.7 μm) decreased from 30 to 5 mg in that period. At the same time, a sedimentation process was observed to the floor of the pond, with pesticide loads in bottom sediment rising to about 100 mg (Fig. 10b), almost half of the load in the initial runoff.

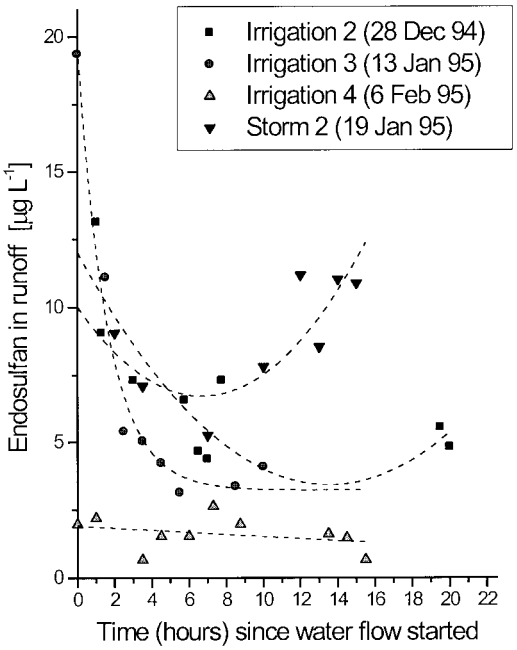

Fig. 8. Endosulfan concentrations in irrigation and storm runoff samples collected at the outlet of Field 4, Auscott Warren. Residues leaving the field decrease with time except for the runoff of a large storm (181 mm).

DISCUSSION

The main focus of this three-year research was on dissipation of endosulfan from cotton fields and its movement off-field through irrigation and storm runoff in the growing regions of northern New South Wales. Apart from the small amounts of endosulfan that miss the target cotton crop and drift downwind (Woods et al., 2001), the results of this study strongly support the view that the majority of endosulfan losses on-field occur by volatilization in the first week after spraying. This applies to both losses from the cotton plants as well as from the soil beneath, and may explain how traces of this chemical have been found in areas never sprayed such as the Arctic (Jantunen and Bidleman, 1998) and around the world (Simonich and Hites, 1995).

The first implication of this fact is that decay curves of parent compounds, α- and β-endosulfan, in both plants (foliage) and soil do not conform with the typical first-order kinetic curves found in most laboratory trials on

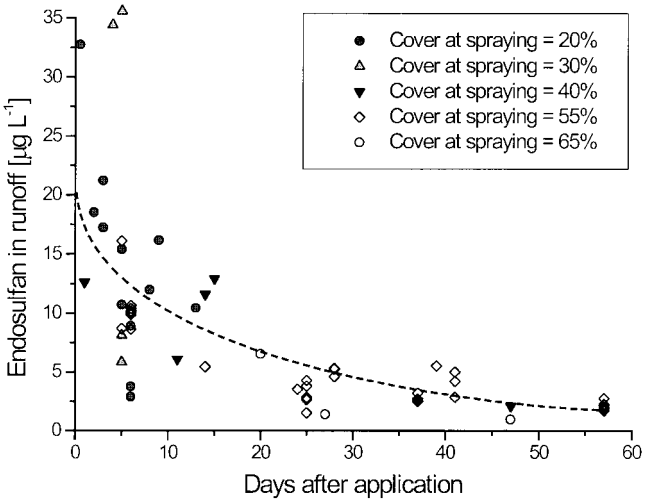

Fig. 9. Endosulfan residues in runoff from 19 outlets of cotton fields at Auscott Warren (1995–1996). The decline in endosulfan concentrations in irrigation runoff is well correlated with the declining residues in soil as crop canopy cover increases at the time of application.

Table 7. Transport of endosulfan residues in runoff water. For each event, the percentages of endosulfan transported are calculated with reference to the residues actually on-field at that time, while the total figures refer to the total amount of pesticide applied in the entire season.

Event	Date	Days since last spraying	Discharge	Endosulfan in water	Endosulfan removed	Endosulfan removed
			ML ha^{-1}	μg L^{-1}	g ha^{-1}	%
Field 4, Season 1994–1995						
Spraying 1	2 Dec. 1994					
Irrigation 1†	8 Dec. 1994	8	0.97	7.65	7.42	4.3
Spraying 2	21 Dec. 1994					
Irrigation 2	28 Dec. 1994	7	0.84	6.98	5.86	2.9
Storm 1†	5 Jan. 1995	15	0.037	6.11	0.23	0.1
Spraying 3	7 Jan. 1995					
Irrigation 3	13 Jan. 1995	6	0.69	6.96	4.8	2.7
Storm 2	19 Jan. 1995	12	2.35	8.85	20.8	9.9
Storm 3	28 Jan. 1995	21	0.022	6.09	0.13	0.07
Irrigation 4	6 Feb. 1995	30	1.03	1.62	1.67	0.9
Irrigation 5†	20 Feb. 1995	44	0.73	0.75	0.55	0.3
Irrigation 6†	4 Mar. 1995	56	0.75	0.15	0.11	0.08
Total			7.42		41.57	1.9
Field 20, Season 1995–1996						
Spraying 1	30 Nov. 1995					
Spraying 2	14 Dec. 1995					
Irrigation 2	20 Dec. 1995	8	0.67	24.15	16.18	1.8
Spraying 3	23 Dec. 1995					
Storm 1	1 Jan. 1996	8	0.009	2.91	0.03	0.003
Spraying 4	9 Jan. 1996					
Irrigation 3	13 Jan. 1996	6	0.59	10.57	6.24	0.6
Storm 2†	19 Jan. 1996	11	0.7	11.01	7.71	1.1
Irrigation 4†	31 Jan. 1996	22	0.54	8.58	4.63	1.1
Irrigation 5	17 Feb. 1996	39	1.06	4.86	5.15	1.6
Irrigation 6	6 Mar. 1996	58	0.7	2.14	1.5	0.3
Total			4.27		41.44	1.5

† These are calculated values based on regression lines fitted to the field data.

endosulfan (Beard and Ware, 1969; Ghadiri et al., 1995) and other pesticides. Instead, dissipation of endosulfan from a crop occurs in two phases, the first of which reflects the rapid volatilization of α-endosulfan and to a lesser extent that of β-endosulfan, with little amounts (<10%) degraded into the sulfate product. It seems that most research on the plant degradation of this insecticide carried out previously (Finlayson and MacCarthy, 1973) did not observe this fact, perhaps because most of the early dissipation occurs in a very short period of time. Certainly in foliage, the calculated half-life of endosulfan parent isomers in this first phase is 1 to 2 d, and this is about five times shorter than in soil (3–10 d). Only by intensive sampling and measuring the amounts of endosulfan escaping the field was it possible to correlate the fast disappearance observed in the first week with volatilization (see Fig. 3 and 4).

After the first week, there is a noticeable lessening in rates of dissipation, particularly that of α-endosulfan (see Fig. 4 and 7), while no more volatilization appears to occur once surface concentrations are dissipated. Dissipation of endosulfan from this time onward (second

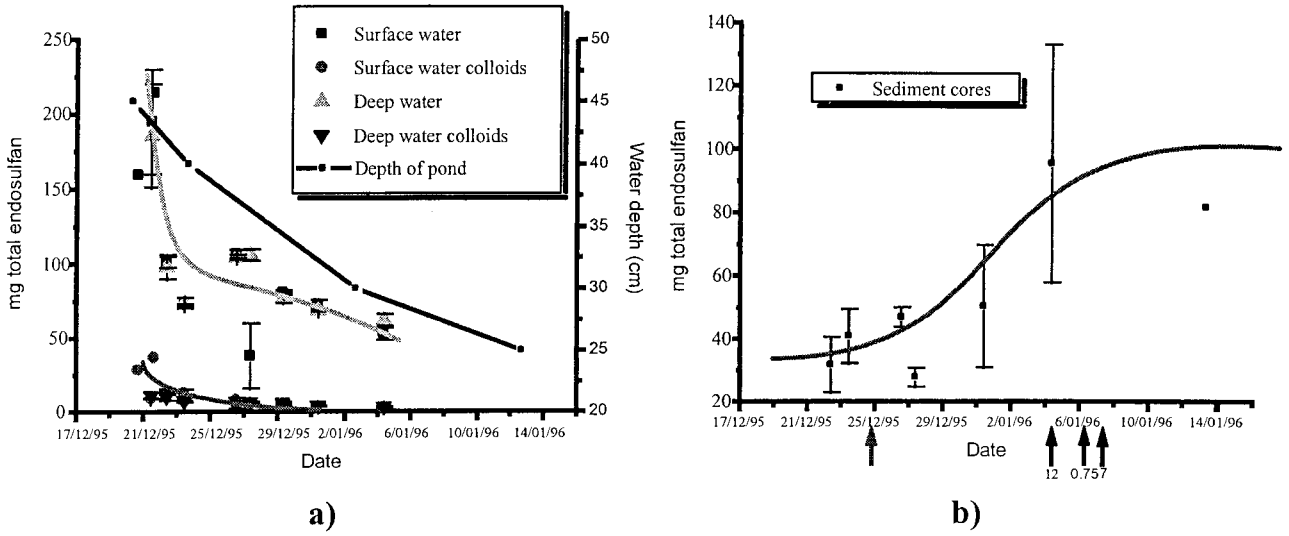

Fig. 10. Dissipation of endosulfan in ponded irrigation water and suspended particulate (*a*), and build-up of endosulfan residues on the pond-floor sediments (*b*). Arrows indicate water inputs from rainfall.

phase) must be due mostly to degradation in plant material and soil, with losses in runoff water being minimal and not accounting for more than 1.5 to 2% of the total insecticide applied on one field during the growing season. The feature of this phase is a three to five times longer half-life of both parent isomers in foliage and also for β-endosulfan in soil, whereas much longer persistence about 20 times greater for α-endosulfan in soil was estimated. As a consequence, the normal degradation processes in soil result in an average half-life of 69 d for α-endosulfan and 46 d for β-endosulfan, both of which are much shorter than those reported previously (Stewart and Cairns, 1974; Rao and Murty, 1980). Less persistence in soil of β-endosulfan has also been observed by some authors (Ghadiri et al., 1995), and could be explained by the conversion of this isomer to endosulfan sulfate in aqueous media (Southan and Kennedy, 1995). The longer persistence of α-endosulfan in soil, foliage, and trash, however, suggest that this isomer is not as liable to degradation as β-endosulfan, particularly in the presence of water.

Endosulfan, including the sulfate, is quickly metabolized by the cotton plants, with only 2 to 3% of the amount applied in one spraying remaining in the foliage after 2 wk. However, small amounts of endosulfan remain in the plant tissues of foliage after harvesting (but not lint), with concentrations of 0.5 mg kg^{-1} six months after spraying, and an estimated half-life of 65 d, very similar to that found in soil residues. This residue is firmly bound to the organic material, and can be found in the gin trash, being consistent with endosulfan's high K_{ow} (Hornsby et al., 1996).

It is apparent that early sprayings account proportionally for most of the pesticide found in soil, while the closer the time gap between pesticide applications the greater the build-up in soil residues that will occur. The observed peak patterns in soil after consecutive applications (see Fig. 7) are consistent with modeling developed by other authors involved in this research program (Connolly et al., 2001). Apart from the even distribution of residues across the field, differences in endosulfan deposition were observed between the tops of beds and the furrows in the first 3 d after application, but they disappear in time. Transport of residues by runoff water was discarded as an explanation for migration across the soil profile since no irrigation or rainfall occurred in the 3 d after spraying, during which sampling took place. It is also likely that the pattern of deposition on the field was affected by the wind direction and bed architecture, so that one side of a furrow initially could have less residues than the other. This was confirmed on the second year at Field 4, where two sets of paper strips placed on the top beds, slope, and bottom of furrows revealed that pesticide deposition was consistent with the wind direction at the time of spraying. These measurements were performed during two applications, and it became apparent that some shading effect from cotton plants was also a factor in the differences of micro-distribution observed.

Dissipation of endosulfan from soil, however, depends to a large extent on the degradation of the sulfate metabolite, for which a half-life of 92 ± 47 d has been calculated. Oxidation of the parent compounds causes an initial build-up in the sulfate product, which reaches a peak between a week and a month after the last application. Consecutive applications result in some endosulfan residues remaining in soil for much of the year and decreasing slowly until the start of the next spraying season, when residue levels fall close to the detection limit. Other data indicate that endosulfan sulfate is formed exclusively through biological oxidation in plant tissues and by soil microorganisms (Martens, 1977; Guerin and Kennedy, 1992) or collembola (Park, 2000). There is no evidence of its formation by chemical oxidation in pure water, though some studies have reported formation in river water to levels that do not exceed 5% of the initial amount (Peterson and Batley, 1993).

Endosulfan in runoff is found mainly in the non-sedimentable soluble fraction (80%), the remaining residues being most likely bound to the soluble colloids and suspended sediment (Peterson and Batley, 1991). It is important to draw attention to the fact that concentrations of endosulfan in runoff water depend entirely on the residue amounts present in soil during an irrigation or storm event. These amounts are much greater early in the spraying season, when concentrations in soil are highest as a result of spraying on low plant canopy cover. Thus, the risk of significant contamination is the greater. During the first irrigation event, the advancing water front sweeps pesticide from the top layer of soil, moving it to the tail drain. Once the soil has wetted there is no extra pesticide removal by the water running behind, all runoff water being contaminated to a similar extent. Where the slope of furrows increased toward the end near the tail drain (Field 4, Warren), there was a noticeable increase in the sediment load and the total pesticide transported.

In agreement with other authors (Littleboy et al., 1992; Ghadiri and Rose, 1993), it appears that endosulfan residues are removed from the top soil and deposited along the tail drains. Residue levels in cores from the tail drain suggest that in the first runoff of the season the pesticide from the top soil layer is removed and carried down to the tail drain, where it settles before the water goes through the outlet. In subsequent irrigations, runoff water may then remove this contaminated deposit from the tail drains so as to increase the endosulfan loadings at the outlet. The tail drain would act as a temporary buffer avoiding the high pesticide loads of early sprayings that go directly into the return drains with the first runoff.

In normal conditions, irrigation waters account for 1 to 1.5% of total endosulfan transported off-field in one year. However, the total endosulfan removed from a field by runoff also depends on the total volume of water discharged. For instance, major storms may be capable of transporting up to 10% of the endosulfan on-field at the time of the event, particularly if they occur soon after an endosulfan application. During this research, a 181-mm rainfall caused the loss of 1.2 kg of endosulfan in 130 ML of runoff. Had this major storm event occurred the day after the endosulfan application, the

same percentage of pesticide residues would have resulted in the transport from the field of about 2.5 kg of residues.

The presence of significant levels of endosulfan sulfate in river systems during the growing season (Cooper, 1996) could be to a certain extent the result of runoff discharged into river after big storm events. As fish are extremely sensitive to low concentrations of this chemical—LC_{50} in the range 0.2 to 11 $\mu g\ L^{-1}$ (Sunderam et al., 1992), and typical concentrations of endosulfan in storm runoff are between 2 and 10 $\mu g\ L^{-1}$, endosulfan can become a serious environmental problem unless effective measures to avoid spillages of this sort are implemented. Containment of storm runoff, therefore, seems to be crucial to avoid contamination of rivers and waterways (Hugo et al., 1996). In this regard, the building of large storages for water ponding of storm runoff may help the degradation of waterborne residues, since the half-life of endosulfan in water was found to be only 2 to 8 d, consistent with that found in the literature (Barry and Logan, 1998). However, ponding of water causes the sedimentation of endosulfan sulfate in sediments at the bottom, which undergo a very slow degradation (Kimber et al., 1996).

Chemical Balance

Based mainly on the complete data sets from Fields 4 and 20, it can be stated confidently that dissipation of endosulfan from a cotton field occurs mainly through volatilization (approx. 70%, mostly as α-endosulfan), with only a small percentage (8.5%) remaining on-field a month after the last spraying (95% in soil and 5% on plants). Since the endosulfan losses through runoff during the entire growing season account for less than 2% of the total pesticide amount applied, degradation in either plants or soil microorganisms should be held responsible for the disappearance of the majority of endosulfan residues on-field, which amount to 25 to 30% of the total applied. By the start of the following spraying season, only 1% of the endosulfan initially applied remains in the soil, most as the sulfate oxidation product, with very little residue build-up between years.

CONCLUSIONS AND RECOMMENDATIONS

Despite the rapid dissipation by volatilization and degradation of most of the endosulfan applied to cotton fields in the first few weeks after application, the remaining residues require careful management if significant contamination off-farm is to be prevented. Sufficient residues were found in plant material to pose a risk if cotton plants are used to feed stock. The decision of the cotton industry in 1995 to prohibit the feeding of cotton trash to livestock since this program began—mainly as an outcome of beef contamination with chlorfluazuron (Helix)—is therefore very soundly based. It is preferable to allow foliage to degrade on cotton fields, ensuring pesticide breakdown.

The study has shown that an important factor in the extent of environmental risk is the degree of soil exposure during pesticide application. Thus, high cover from the cotton canopy can mitigate against high concentrations of pesticide in soil and the pesticide load in runoff. The advent of transgenic Ingard cotton, not requiring 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 sulfate, which 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. Consequently, as far as possible irrigation and storm runoff must be retained on-farm by proper management of water including the provision of the maximum water storages. In very large storms 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. Unfortunately, endosulfan sulfate on sediments degrades too slowly, even in ponded water, to allow deliberate release of untreated water from farms to river systems.

The results of this study focused on endosulfan have already found application in the development of best management practices by the cotton industry (Williams, 1998). By requiring better water management on farms and techniques such as band spraying to reduce the extent of soil contamination, significant reduction in the risks to the off-farm environment have been obtained.

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