THE FATE OF ENDOSULFAN SPRAYED ON COTTON

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Abstract

An extensive analysis of the total burden of endosulfan in cotton growing soils has been conducted over the past three years on four cotton fields in the Namoi valley of northern New South Wales. The study indicates that the maximum total burden of endosulfan residues, for analyses conducted at about 6-weekly intervals through the year, is usually not greater than a single application of endosulfan (750 g a.i./ha). This declines to lower levels at other times and particularly when cotton is rotated with wheat. There is no evidence that endosulfan residues are accumulating with current spraying rates; volatilisation is proposed to be a major cause of dissipation of endosulfan. Despite these findings, the concentrations of endosulfan in soil detected, particularly during the spraying season, are significant and could pose an environmental threat if transported off-farm in return waters.

Introduction

Endosulfan, a sulphurous acid ester of a chlorinated cyclic diol, plays an important role in the Australian Insecticide Resistance Management strategy, used by the Australian cotton industry. Commercial formulations consist of a mixture of two isomers, alpha (α) and beta (β) endosulfan in the ratio 70:30, and are commonly used in Australia as an emulsifiable concentrate (EC) or as an ultra-low volume formulation in vegetable oil (ULV). It is used for the control of the cotton bollworm and native bud-worm (*Helicoverpa/Heliothis* spp.), thrips, loopers, and aphids on cotton (Whyte and Conlon, 1990).

Endosulfan diol formation has been shown to result from either chemical, biological, or photolytic processes. Chemical hydrolysis is a pH dependent process, with the rate of reaction increasing with increasing pH (Cotham and Bidleman, 1989). Archer *et al.* (1972) observed diol formation and to a lesser extent, the production of endosulfan hydroxy-ether, lactone and ether after exposure of endosulfan in thin films of endosulfan to UV light. Guerin and Kennedy (1992) reported endosulfan diol to be the major product of endosulfan incubated with anaerobic bacteria. Endosulfan sulphate production was shown by Martens (1977) to be carried out by soil fungi. Its formation was about three times higher under aerobic conditions than anaerobic.

Whilst endosulfan does not accumulate in the body fat of animals and has not been shown to bio-accumulate, it is perceived to represent a threat to the environment. Endosulfan exhibits low mammalian toxicity (LD_{50} of α-endosulfan 76 mg/kg; of β-endosulfan 240 mg/kg and of endosulfan sulphate 76 mg/kg) but is highly toxic to fish (LD_{50} of α, β and sulphate 0.1-10 µg/kg) whilst the other breakdown products are relatively non-toxic to fish (diol, ether, hydroxy-ether and lactone 1-10 mg/kg) (Goebel *et al*., 1982). Sunderam *et al.* (1992), in studies on native fish, reported 96hr LC_{50} values in the range 0.2 to 11.4 µg/L for the parent compounds. Endosulfan residues in this range of concentration have periodically been found in river water of northern NSW during the cotton growing season (Preece and Whalley, 1993).

A number of questions have been examined during this study on the environmental fate in soil of endosulfan sprayed on cotton. These include an analysis of the total burden of endosulfan residues in soil; whether endosulfan is accumulating in cotton-growing soils year by year; how rapidly endosulfan dissipates from soil and which breakdown products are formed. Answers to these questions are of importance in deciding whether this pesticide may continue to be used for cotton-growing under Australian conditions.

Materials and Methods

Field sites

Soil sampling was carried out at four field sites, two at Auscott, Narrabri (fields 16 and 33) and from one field at each of two smaller farms near Wee Waa (sites 3 and 4). Both smaller farms employed a 1 m bed system for the growth of cotton, while Auscott has employed 2 m permanent beds.

Soil sampling

Soil samples were taken with a stainless steel corer (6.25cm diameter) to depths of 5, 10 or 20 cm. Field sampling, scheduled independently of spraying events, was based on a semi-random zigzag design, with buffers of 50 m used around the perimeter of the fields (Jackson, 1958). Soil cores were either carefully pre-mixed in a glass tray and sub-sampled (in the case of the deeper samples) or collected whole into 250 mL wide-mouth glass jars. Jars were lined with aluminium foil and cooled with frozen gel packs during transport to a deep freeze. Unless otherwise stated, soil cores were taken from the sloping edge of the bed for the 1 m bed system, or from either side of the plant in the 2 m bed system.

Chemicals and glassware

All endosulfan standards (α-endosulfan (99.8%), β-endosulfan (99.8%), endosulfan ether(98%), endosulfan diol (98%), endosulfan hydroxy-ether(EHE)(98%), endosulfan lactone (98%) and endosulfan sulphate (98%)), were gifts from Dr. Klaus Stumpf, Hoechst AG, Frankfurt am Main, Germany, and Hoechst Australia Limited. Solvents used in extraction and analysis were Nanograde (Mallinckrodt). Neutral alumina of 80-120 mesh size (BDH Chemicals and Rhone Poulenc), was heated at 600˚C for 6hr and made to 7% w/w with deionised, distilled water. Sodium sulphate was of Analytical Reagent grade (BDH chemicals) and was heated at 500˚C prior to use. Both the alumina and sodium sulphate were stored in desiccators over silica gel. Glassware was borosilicate glass, washed in a solution of Pyroneg detergent (Diversey Australia Pty Ltd.) and rinsed with tap water followed by a rinse with nanograde hexane immediately prior to use. Evaporations were carried out using a Zymark Turbo-Vap® 500 at 45˚C bath temperature with solvent collection.

Storage and extraction of soils

Soil samples were stored in 250 mL clear glass jars with aluminium foil lined plastic lids. Exposure to light was avoided and the jars were stored in a deep freeze at -20˚C. The jars contained a sub-sample in the case of the 20 cm cores and the whole sample in the case of 5 and 10 cm cores. Samples were thoroughly hand mixed by spatula prior to sub-sampling 25 g

into a 250 mL Quick-fit conical flask. A further 10 g sample was weighed accurately for moisture determination.

The soil was extracted in 150 mL of 25% acetone in dichloromethane. Samples were shaken overnight at 165 rpm on a Braun Certomat® orbital shaker. A 75 mL sub-sample was filtered through anhydrous sodium sulphate and evaporated to 1mL volume using the Turbo-Vap. This sample was applied to a clean-up column containing 7 g of alumina topped with 1g anhydrous sodium sulphate. The column was eluted sequentially with 60mL hexane followed by 60 mL 25% acetone in hexane. This procedure was verified experimentally. The fractions were combined and the volume reduced to about 1 mL then made up to 10 mL in hexane for analysis.

Gas chromatographic analysis

Samples were analysed on a Hewlett-Packard 5890II gas chromatograph fitted with 7673 auto sampler using ^{63}Ni electron capture detection and a Hewlett-Packard 5971 mass selective detector for confirming the identity of selected peaks. Columns used were J&W DB-17, 30 m, 0.320 mm internal diameter, 0.25 μm stationary phase thickness, fused silica capillary for ECD work and J&W DB-5, 30m, 0.320mm, 0.25μm phase thickness, fused silica capillary for mass spectral work.

Splitless injections of 2 μL were made with the injection port purged at one minute. Helium carrier gas velocity was set at 40 cm/second at mid-run temperature. Temperatures used were: injection port, 280˚C; detector, 300˚C; oven 55˚C for 1 minute, 60˚C/ minute to 180˚C, then 4˚C/minute to 250˚C, hold for 10 minutes then 10˚C/ minute to 260˚C. Quantification was carried out using Hewlett-Packard 3365 software, based on peak area using external standards. Recalibration was carried out every seven injections.

Sampling studies

All results are expressed as micrograms per kilogram (mg/kg) on a dry weight basis.

In the major study, involving the determination of seasonal profiles of endosulfan residues over several calendar years. Soil samples were taken to a depth of 20 cm up to February 1992 and to 10 cm subsequently, once the vertical stratification had been established in the field.

The vertical stratification of the α- and β-isomers and endosulfan sulphate was investigated. Soil cores sectioned into four 5 cm layers were taken from field site 3 near Wee Waa, which operated under a 1 m bed system. In this study samples were taken in line with the plants, on top of the bed.

Results

Dissipation of endosulfan from cotton-field soils

In Figure 2 is shown a seasonal profile of the concentration of endosulfan residues in the soil of a cotton-field. No attempt was made to relate soil sampling to dates of spraying in order to achieve a regular sampling schedule throughout the year. Endosulfan sprays (approximately three to six) were carried out during the period from mid-November to early February, in response to insect pressure. The time 'window' for the spraying of endosulfan under the Insecticide Resistance Management Strategy ended on the 13th of February (Forrester, 1990).

The first soil sampling was obtained prior to the season's first endosulfan application. A significant concentration of endosulfan sulphate in soil prior to spraying (0.067 mg/kg) was observed as a residue from applications in previous seasons. Endosulfan sulphate concentrations increased markedly during the spraying season, indicating a rapid conversion from either the α- or β-isomers in cotton-fields.

Although α-endosulfan is the major constituent in the formulation applied (70%), it was always of the lowest concentration compared to β-endosulfan and endosulfan sulphate. α-endosulfan concentrations were significant only during the spraying season, and never greater than 0.04 mg/kg in the top 20 cm of the soil, unless soil is sampled immediately after spraying or only the surface layer (1-2 cm) is sampled. This shows that α-endosulfan rapidly dissipates from the soil, possibly by volatilisation, although conversion to endosulfan sulphate or to the β-isomer could also be a significant process of dissipation.

Also shown in Figure 2 are analyses for other, relatively non-toxic, breakdown products of endosulfan; endosulfan ether, endosulfan hydroxy-ether and endosulfan diol. With the exception of the hydrolysis product, endosulfan diol, these appear relatively insignificant.

From the data in Figure 2, apparent 'half-lives' have been calculated for the sampling in the period 23rd January 1991 to 25th July 1991. The data gave a good fit to a first-order process, indicating -'half-lives' in the field of 43 days, 76 days, and 101 days respectively, for α-endosulfan, β-endosulfan and endosulfan sulphate respectively. These results contrast with the work of Stewart and Cairns (1974), who worked under cool conditions on a Canadian soil and achieved figures of 60 days for α-endosulfan and 800 days for β-endosulfan.

Distribution of endosulfan with depth

The distribution with depth of the major endosulfan residues is shown in Figure 3. The majority of the residues are found in the top 5 cm of soil, indicating that endosulfan is not significantly leached in these grey-cracking soils.

Effects of rotation with wheat

The effect of including wheat in a rotation with cotton is shown in Figure 4. Wheat was planted following cotton in 1991 and cotton was not planted following harvesting of wheat. Subsequently, endosulfan was not applied between mid-February, 1991 and December 1992. From April, 1, 1992, soil cores of 10 cm depth (instead of 20cm) were taken, raising the sensitivity of the analysis by a factor of almost two, since little or no residues were observed below 10 cm depth (see Fig. 3).

A significant decline in residues is obvious in the season when no endosulfan is applied, with expected residue concentrations re-appearing in the following spraying season.

Discussion

This study has demonstrated that endosulfan sulphate, the oxidation product of the two parent endosulfan isomers, is the more persistent residue found in these cotton growing soils. The ratio of the α- and β-isomers present in the formulation applied is not reflected in the field data, indicating rapid conversion or loss by other means, particularly of the α-isomer. Ratios of the isomers similar to those in the spray might be observed only in very shallow soil samples taken immediately after spraying. However, the possibility that endosulfan is particularly prone to runoff immediately after spraying needs further consideration. The major cause for the loss of the α-isomer is probably volatilisation, but also with some conversion to β-endosulfan or sulphate. The vapour pressure of α-endosulfan is 0.006 Pa, with the β-isomer

half that figure at 0.003 Pa (Cotham and Bidleman, 1989). The high volatility of the α–isomer has also been demonstrated in other studies (Beard and Ware, 1969; Archer *et al.*, 1972; Singh *et al.*, 1991; Guerin and Kennedy, 1992).

In this study soil cores were initially taken to 20 cm depth to include the whole of the cultivated soil layer. The aim was to obtain data on the total pesticide burden of these soils, to determine if residues were accumulating. When permanent beds are employed, such deep sampling is clearly not necessary for endosulfan residues, as indicated in Figure 3. However, the depth of sampling needs to be carefully considered for the practical purpose of particular assays. In the current study, the emphasis has been on the total soil burden of residues.

Data from the study of distribution with depth demonstrates that endosulfan does not pose a threat to the environment via the path of leaching into the water-table. However, cultivation, bed forming and the movement of top soil down cracks are possible mechanisms for movement in soil below this level. Hoechst (1990) stated that endosulfan residues do not penetrate the soil to a depth of more than 15 cm. Kimber (1990) observed that β-endosulfan did not leach to a greater depth than 13 cm in a sandy loam, consistent with the data for the grey-cracking soils in the current study. An implication of the dissipation with depth study is also that the sensitivity of analysis can be increased by sampling shallower cores. However, it is necessary to consider the accuracy to which soil samples can be practically taken. Shallow samples have proven to be difficult to take reliably on these cracking-clays. Swelling and shrinking are significant processes in this soil type. Early samples were taken to a depth of 20 cm to ensure inclusion of the whole of the cultivated layer. However, the use of permanent beds in some cases removes the need to sample to this depth.

The soil analyses indicate that endosulfan diol is sometimes a prominent breakdown product. This could reflect the condition of soils, particularly soil moisture status. Previous work has shown that endosulfan diol is formed chemically by hydrolysis in alkaline conditions (Peterson and Batley, 1993) and under anaerobic conditions in aqueous systems in the laboratory (Guerin and Kennedy, 1992). Compared to endosulfan sulphate, the diol is environmentally preferable because of its relatively non-toxic property. It would be of interest to study further the formation of this degradation product. Other degradation products are less prominent, possibly representing temporary intermediate forms as conversion to other non-extractable products occurs.

The rate of dissipation of endosulfan in these soils under field conditions is sufficient to prevent long term accumulation of its residues. Several applications of endosulfan were made in the each growing season. However, the total amount of endosulfan residues never exceeded a single application (750 g active ingredient per hectare over ten or twenty centimetres depth of soil). The concentration of toxic residues in the soil is nonetheless significant and if released to the riverine environment could pose a threat to biota such as fish. Adequate management of soil and water on cotton farms is required to prevent transport off-farm to minimise this threat.

In Figure 4, a more extended soil analysis is shown for Auscott field 16. At this site cotton was grown and sprayed with endosulfan in the first season (sampling dates 3/11/90 to 15/4/91), but was rotated with wheat in the following winter and no endosulfan was applied until the summer of 1992-93. At sites with continuous cotton cropping, endosulfan residues in soil, particularly of endosulfan sulphate were usually significant prior to the commencement of the next spraying season (around 0.1 mg/kg over 20 cm sampling depth). In the rotation with wheat, endosulfan sulphate residues fell to a very low level of about 0.03 mg/kg, supporting the conclusion that endosulfan will not continually accumulate under current Australian cotton-growing practices.

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References

Archer, T.E., Nazer, J.K. and Crosby, D.G. (1972). Photodecomposition of endosulfan and related products by ultraviolet radiation. *J. Agric. Food Chem.* **20**, 954-956.

Beard, J.E. and Ware, G.W. (1969). Fate of endosulfan on plants and glass. *J. Agric. Food Chem.* **17**, 217-220.

Cotham Jr., W.E. and Bidleman, T.F. (1989). Degradation of malathion, endosulfan, and fenvalerate in seawater and seawater/sediment microcosms. *J. Agric. Food Chem.* **37**, 824-828.

Forrester, N. (1990). Pyrethroid resistance strategy change. *Aust. Cott. Grower* **11**, 68-69.

Goebel, S.G., Gorbach, S.G., Knauf, W., Rimpau, R.H. and Huttenbach, H. (1982). Properties, effects, residues and analytics of the insecticide endosulfan. *Res. Revs.* **1**, 1-122.

Guerin, T.F. and Kennedy, I.R. (1992). The anaerobic biodegradation of endosulfan by mixed cultures of soil microorganisms isolated from sediments. pp. 317-323 *In* Klein, J. (Ed) *Soil Decontamination Using Biological Processes*. DECHEMA, Karlsruhe, Germany.

Hoechst. (1990). *Thiodan Product Manual: Up-to-date Facts on Properties and Behaviour-1990.* Hoechst Aktiengesellschaft Marketing Agriculture.

Jackson, M.L. (1958). *Soil Chemical Analysis*. Prentice Hall, Inc., Englewood Cliffs, NJ. USA, 22-28.

Kimber, S.W.L. (1990). *The movement of aldrin, dieldrin and endosulfan in soils.* Honours thesis (BScAgr), The University of Sydney.

Martens, R. (1977). Degradation of endosulfan-8-9-14C in soil under different conditions. *Bull. Environ. Contam. Toxicol.* **17**, 438-446.

Miles, J.R.W. and Moy, P. (1979). Degradation of endosulfan and its metabolites by a mixed culture of soil microorganisms. *Bull. Environ. Contam. Toxicol.* **23**, 13-19.

Peterson, S.M. and Batley, G.E. (1993). The fate of endosulfan in aquatic ecosystems. *Environmental Pollution* **82**, 143-152.

Preece, R.M. and Whalley, P. (1993). Central and North Western Regions Water Quality Program. 1991/92 pesticide monitoring, NSW Department of Water Resources (TS93.094).

Singh, N.C., Dasgupta, T.P., Roberts, E.V. and Mansingh, A. (1991). Dynamics of pesticides in tropical conditions. Kinetic studies of volatilisation, hydrolysis and photolysis of dieldrin and α and β-endosulfan. *J. Agric. Food Chem.* **39**, 575-579.

Stewart, D.K.R. and Cairns, K.G. (1974). Endosulfan persistence in soil and uptake by potato tubers. *J. Agric. Food Chem.* **22**, 984-986.

Sunderam, R.I.M., Chdng, D.M.H. and Thompson, G.B. (1992). Toxicity of endosulfan to native and introduced fish in Australia. *Envir. Toxic. Chem.* **11**, 1469-1476.

Whyte, R.J. and Conlon, M.L. (1990). *The New South Wales Cotton Industry and the Environment*. State Pollution Control Commission, Sydney, TR 90/9

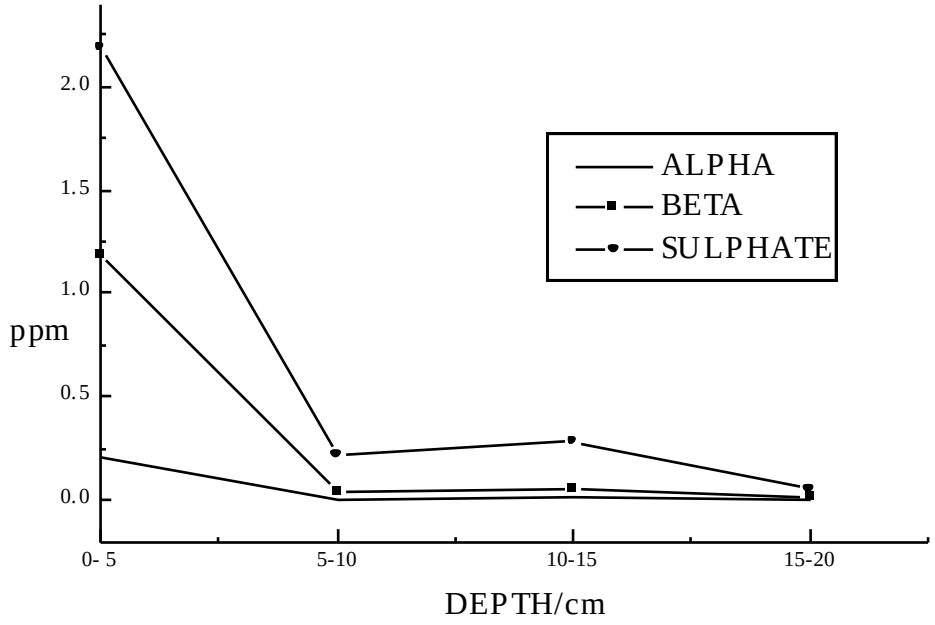

Figure 1. Endosulfan and its five breakdown products. Pathway after Miles and Moy (1979).

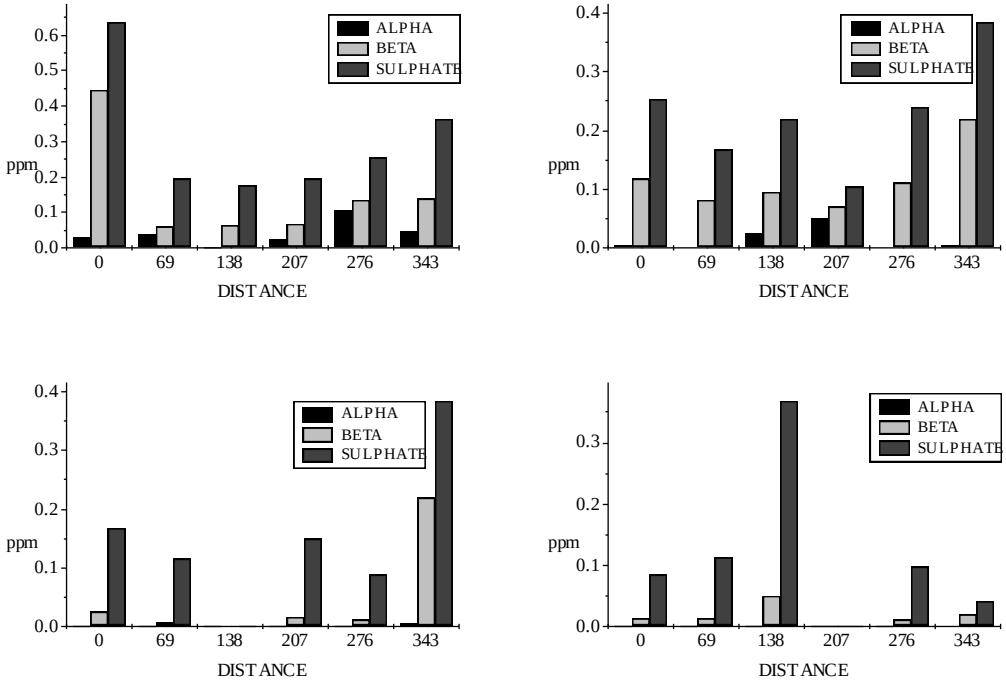

Figure 2. The distribution of endosulfan with depth in soil. Results of a single core stratified into four 5cm layers. Samples taken from field site 3.

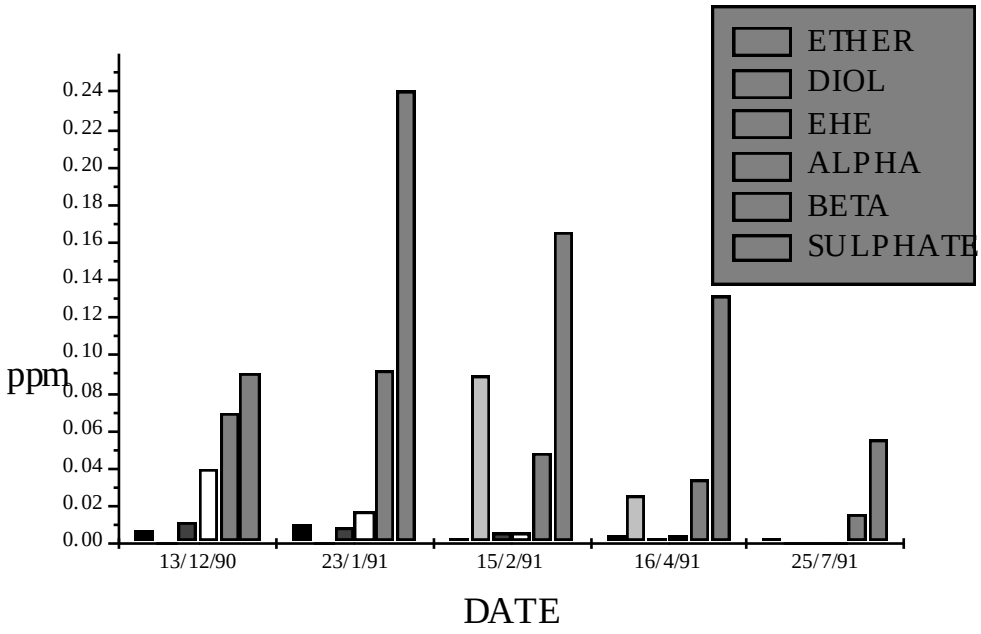

Figure 3. Seasonal soil burden of endosulfan residues. Soil cores of depth 20cm were taken over an eight month period from 3/11/90 to 25/7/91. Each data point is based on 20 individual samples. Samples taken from field site 4.

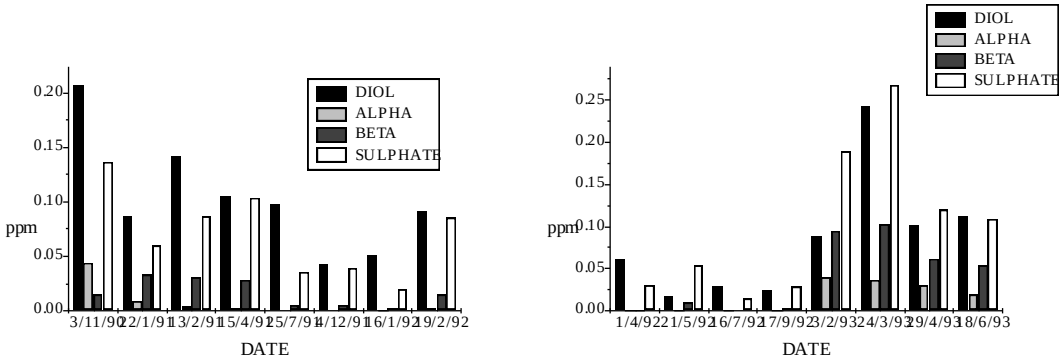

Figure 4. Seasonal soil burden of endosulfan residues for Auscott field 16. From 3/11/90 to 19/2/92 cores were taken to 20cm depth and from 1/4/92 to 18/6/93, taken to 10cm depth. Cotton was grown in the 1990/91 season and in the 1992/93 season. In the 1991/92 season, wheat was grown in the winter and no endosulfan was applied.