

CONTROLLED ENVIRONMENT STUDY OF THE DEGRADATION OF ENDOSULFAN IN SOILS

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Abstract

The degradation rate of endosulfan applied to a Black Earth soil from South East Queensland, was studied in controlled environment chambers. The degradation rates of α - and β -endosulfan were determined for the soil samples kept at the constant temperature of 30°C under two water contents of 20% and 30% and submerged under water. The degradation rates of both isomers in all three moisture conditions followed first order kinetics with the rate constants differing significantly between submerged and non-submerged soils. For non-submerged soils the degradation rates of the two endosulfan isomers were lower for the soil with higher water content. The β -endosulfan isomer disappeared from the samples at a faster rate than the α -isomer at both water potentials. However the rates of decline for both isomers were much slower than those suggested in the literature.

Degradation of both endosulfan isomers in the submerged soil took place at a slower rate than in the non-submerged conditions, and in contrast to the results with unsaturated soil, the rate for β -endosulfan was slower than the α -isomer. Adding endosulfan to soil appears to reduce the rate of degradation of other organochlorine pesticides already present in the soil. The half-life of dieldrin was significantly increased in the presence of endosulfan. This effect was much more pronounced at the higher of the two water contents investigated. The applicability of these results to the soils of cotton farms in Queensland and NSW is under investigation.

Introduction

Amongst the 40 or so different insecticides, herbicides, conditioners and defoliants registered on cotton, endosulfan is the most commonly used (Barrett *et al.*, 1991). It has been in use for more than three decades, being first introduced as a replacement for the highly persistent DDT. Compared to DDT, aldrin and dieldrin, which are now banned from agricultural use, endosulfan is commonly assumed to be much safer for the environment since it is less persistent and does not bioaccumulate to the same extent (Peterson and Batley, 1991). With a solubility of 0.3-0.5 mg/l, and a half-life ($T_{1/2}$) in solution of two to three days, endosulfan is not considered as a long term threat to the environment (Barrett *et al.*, 1991). However it is extremely toxic to fish, exhibiting lethality at concentrations as low as 1 μ g/l. Despite its rapid degradation in water, this paper presents data that endosulfan can persist for a relatively long period of time when bound to soil particles, which can be a source of contamination at later stages.

Endosulfan is a mixture of two isomers, α -endosulfan and β -endosulfan, in a ratio of 7:3 with α -endosulfan said to be more volatile than β -endosulfan. Worthing (1983) reports the figures of 0.32 mg/l and 0.33 mg/l for the solubility in water at 22°C of α - and β -endosulfan respectively, while Willis and McDowell (1982) give a much lower average solubility of 0.05 mg/l for both isomers. Endosulfan is effective against a wide range of insects and certain mites on cereals, coffee, cotton, fruit, oilseeds, potato, tea, vegetable and other crops. It is metabolised in plants and mammals to the corresponding sulphate with a toxicity to fish

similar to endosulfan (the sulphite). Half-life in water and in most fruit and vegetables is reported to be 3-7 days (Worthing, 1983).

β -endosulfan is hydrolysed faster than the α -isomer and the rate for both increases with pH. Hydrolysis seems to be the main initial process in degradation of both isomers at high soil pH values. Under aerobic conditions endosulfan sulfate has been detected as the major metabolite. In flooded soils endosulfan diol seems to be the main metabolite produced closely followed by endosulfan sulfate (Martens, 1977).

The relatively rapid disappearance of dissolved endosulfan in water bodies is accompanied by less knowledge on the fate and the long term effect of the sorbed fraction of this pesticide. One of the objectives of this research was to investigate the persistence, degradation and half-life of newly-added endosulfan to soil, and the influence of soil-water potential on such characteristics. Also discussed here is the interaction between endosulfan and the aged organochlorine pesticides already present in the soil used in these experiments.

Materials and Methods

The physical and chemical characteristics of the soil used in the experiments reported in this paper are given in Table 1. The soil was from a farm in the Beaudesert area of south east Queensland excluded from raising cattle due to high residue levels of pesticides. Pesticide content of the soil before the initiation of the experiments are also given in this Table. Aldrin and dieldrin were already present in the soil and endosulfan was added by soaking samples of soil in acetone solutions containing known concentrations of the pesticide. The acetone was then allowed to evaporate before wetting the soil to the required water content. Sub-samples of this soil were put in sealed jars and transferred to constant temperature cabinets. Samples of wet soil were taken from the jars once every fortnight and extracted immediately using the method described by Ghadiri and Rose (1993).

Gas chromatographic analysis of soil extracts

Analysis of sample extracts was performed with a Varian 3400 capillary column gas chromatograph with split-splitless injector and ECD detector. Column dimension was 0.25 mm i.d. X 15 m in length and 0.25 mm film thickness. Injector and detector temperatures were 220°C and 300°C respectively. The initial column temperature was 50°C and program rate was 50°C/min. The final column temperature of 170°C was held for 30 minutes. Helium and 10 percent argon in methane were used as carrier and make up gases respectively. Flow rate for carrier gas was 24 ml/min and for make-up gas 33 ml/min. A standard mixture of endosulfan, aldrin and dieldrin pesticides at different concentrations were prepared and used to calibrate retention time and to prepare response curves.

Results and Discussion

Effect of soil water content on the degradation of organochlorine pesticides

Figure 1 shows the degradation curves of α - and β -endosulfan for the two soil moisture contents of 20 and 30%. The degradation rate for the α -endosulfan isomer is slower (and the half-life longer) at the higher gravimetric water content of 30% as compared to 20%. Though not statistically significant, the trend is the same for the β -isomer. First order kinetic degradation equations for each of the two isomers for each soil moisture condition are given in Table 2, giving the pesticide half-lives shown in Table 3.

The degradation of two other organochlorines, aldrin and dieldrin, already present in the soil were also investigated (Tables 2, 3; Fig. 2). These results show that the moisture content affects the degradation rates of aldrin and dieldrin in a similar manner to that for endosulfan. Half-lives of both aldrin and dieldrin are substantially higher for 30% water content than 20% (Table 3).

Putting this data on the effect of soil moisture content on half-lives together with that of Ghadiri *et al.* (1995), leads to the following general conclusion applicable to the whole range of organochlorine pesticides studied. This conclusion is that there appears to be a range of water contents suitable for pesticide degradation, but that at both lower and higher water contents (10% and 30% respectively, for this soil), half-lives are increased.

Degradation of endosulfan under constant temperature

Averaged over the two water contents of 20% and 30%, the fitted first order rate equations give half-lives of 33 and 22 weeks for α - and β -endosulfan respectively (Table 3). The half-life of α -endosulfan is smaller but similar to that of the highly persistent aldrin and dieldrin, which is noteworthy and unexpected. Since α -endosulfan forms about 70% of commercially available endosulfan, its characteristics have a dominant effect on the behaviour of the pesticide. Thus it is of interest that endosulfan has been referred to in the literature as one of the less persistent organochlorines. The evidence for endosulfan being less persistent in the soil than the other, now banned organochlorines, seems to stem from the fact that the soluble forms of this pesticide disappear from the water bodies in just a few days (Barrett *et al.*, 1991). However this information provides no guide to the persistence of the sorbed fraction of the endosulfan which forms the bulk of the pesticide residue in the soil and sediment. Ghadiri *et al.* (1995), using the same soil as in the experiments reported here, have reported significantly slower degradation rates for both aldrin and dieldrin in the soil kept under variable outdoor moisture and temperature as compared to those kept under the controlled environment with constant moisture and temperature. If we use the ratio of outdoor to controlled environment half-lives for aldrin and dieldrin reported by Ghadiri *et al.* (1995) as a guide, the half-life of endosulfan under natural conditions could extend to two to three years.

The reasons for such an unexpectedly long half-life for soil-sorbed endosulfan could be the high sorption capacity of the soil used in this study, and its low pH value. As pointed out by Ogram *et al.* (1985), adsorption of both pesticide and microorganisms to soil particles could significantly affect the degradation rate of the pesticide and the degrading capability of microorganisms. The high clay (55%) and organic matter (5.5%) content of the soil used in this study means that both pesticide and microorganisms are strongly adsorbed to the soil possibly rendering pesticide less susceptible to degradation by whatever processes are involved.

Degradation of endosulfan under submerged condition

Figure 3 shows the degradation curves of α - and β - endosulfan in submerged soil at 30°C. Both curves follow, once again, an exponential decline resulting in first order kinetic equations (Equations 1, 2) with high r^2 values.

$$(\alpha\text{-Endosulfan}) \quad C_t = 4.706 \exp(-0.0039t) \quad r^2 = 0.93 \quad (1)$$

$$(\beta\text{-Endosulfan}) \quad C_t = 2.235 \exp(-0.0028t) \quad r^2 = 0.87 \quad (2)$$

The half-lives for α - and β - isomers in submerged soil at 30°C are 34 and 47 weeks respectively. Compared to the half-lives under non-submerged condition (given in Table 3),

α -endosulfan degradation is little affected by submergence, but the β isomer degrades at a significantly slower rate when submerged. These results are unexpected since it is generally assumed that the degradation rates of both endosulfan isomers, as for other organochlorines (Newsom, 1985) are faster under anaerobic than aerobic conditions. Degradation of aldrin and dieldrin in the submerged soil was also significantly slower than in non-submerged soil for the same incubation temperature. When submerged the half-lives of aldrin and dieldrin in soil were 104 and 130 weeks respectively as against 56 and 73 weeks if not submerged.

Effect of added endosulfan on the degradation of aldrin and dieldrin

The effect of a newly applied pesticide on the degradation of sorbed pesticide already in the soil has received only limited study. If the impact of added pesticides is on the activities and population of pesticide-degrading soil microorganisms, this opens up the possibility of multiple interactions between pesticides and soil. While cross enhancement of pesticides has been reported by some (Felsot *et al.*, 1981), most researchers have found that the addition of some pesticides to soil can adversely affect the activities of soil microorganisms in degrading other pesticides already in the soil, resulting in increased soil persistence of such pesticides (Smith, 1982a,b; Roslycky, 1980). Such a negative interaction could be the cause of the reduction in degradation rate of dieldrin when endosulfan was added in these experiments (Fig. 4). The half-life of dieldrin (means of two water contents) was increased in the presence of endosulfan by 46% (Table 3), but the rate of degradation of aldrin was not affected.

It is suggested that the endosulfan applied to the soil might have reduced either the population or the activities of soil micro-organisms responsible for the degradation of the two organochlorine pesticides already in the soil. The adverse effect of added endosulfan on the degradation of aldrin and dieldrin is more pronounced at the higher soil water content of 30%. The presence of high levels of DDE in the Australian cotton soils, several years after their last application (measurement carried out by the author for a related research project), could, to some extent, be due to the effect of applied endosulfan in slowing their degradation rate. The reverse may also be the case, but this research did not deal with this.

Conclusion

Degradation of sorbed endosulfan at constant temperature appears to be well described by a first order kinetics equation under every moisture condition studied. In the soil studied, the degradation rates for both endosulfan isomers, however, are much slower than expected from the literature, half-lives being comparable with those of the most persistent members of the organochlorine family of pesticides. The main reason for such longer-than expected half lives could be the low pH value of the soil used in the experiments. It may be noted that in Australia, though not necessarily elsewhere, cotton soils have a high pH.

The degradation rates of both α - and β -endosulfan in the moist (non-submerged) soils were affected by soil moisture content, both rate constants being smaller for 30% water content than 20%. This effect was more pronounced for α -endosulfan than the β -isomer. Similar effects of water content were observed for aldrin and dieldrin present in the soil. Combining these results with those given by Ghadiri *et al.* (1995) suggests that the soil water content of around 20% (-220 kPa potential) may be the optimum moisture condition for the degradation of endosulfan and other organochlorine pesticides studied. The degradation of all these pesticides decrease when the soil is wetter or drier than this optimum value.

When submerged under a deep layer of water, the degradation of β -endosulfan in soil is significantly slower than in the non-submerged condition, while the reverse was true for the α -isomer. Such an unexpected behaviour of the endosulfan isomers in the submerged soil

necessitates further studies of these chemicals in the bedloads of the rivers and lakes which receive agricultural runoff.

A negative interaction was observed between the newly applied endosulfan and other organochlorine pesticides already in the soil. Applying endosulfan to the soil containing aldrin and dieldrin reduced the rate of degradation of the latter two pesticides. Interactions of this type could become an important factor in predicting the degradation rates and the half-lives of a various sorbed pesticide added to the soil. Interaction of similar nature might have contributed to the persistence of DDT and DDE in the cotton soils of Australia several years after their final application.

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Table 1. Some properties of the soil used in all reported experiments.

Property description	Value
<u>Mechanical analysis</u>	
clay	55%
silt	16%
sand	29%
texture class	clay
Cation exchange capacity	20 cmol kg ⁻¹
pH (1:5 soil-water ratio)	5.84
Electrical conductivity of saturation extract	0.25 S m ⁻¹
Total nitrogen (average)	2.36 g kg ⁻¹
Organic carbon	3.50 g kg ⁻¹
<u>Aggregate size (wet sieving)</u>	
> 2 mm	0.54 kg kg ⁻¹
1-2 mm	0.14 kg kg ⁻¹
0.5 - 1 mm	0.12 kg kg ⁻¹
0.25 - 0.5 mm	0.09 kg kg ⁻¹
0.106 - 0.25 mm	0.06 kg kg ⁻¹
0.053 - 0.106 mm	0.02 kg kg ⁻¹
< 0.053	0.03 kg kg ⁻¹
<u>Pesticide concentration</u>	
Aldrin (inherent)	2.54 µg/g
Dieldrin (inherent)	2.48 µg/g
α-endosulfan (added)	4.20 µg/g
β-endosulfan (added)	2.00 µg/g

Table 2. Degradation rate equations for α - and β -endosulfan, aldrin and dieldrin under controlled environments.

Pesticide	Degradation equation		
	20% water content	30% water content	Mean 20%+30%
α -endosulfan	$C_t = 3.79 \exp(-0.0269t)$	$C_t = 3.61 \exp(-0.0154t)$	$C_t = 3.70 \exp(-0.0210t)$
β -endosulfan	$C_t = 1.94 \exp(-0.0378t)$	$C_t = 1.73 \exp(-0.0281t)$	$C_t = 1.81 \exp(-0.0311t)$
Aldrin	$C_t = 1.92 \exp(-0.0166t)$	$C_t = 1.79 \exp(-0.0124t)$	$C_t = 1.86 \exp(-0.0147t)$
Dieldrin	$C_t = 2.88 \exp(-0.0164t)$	$C_t = 2.59 \exp(-0.0094t)$	$C_t = 2.74 \exp(-0.0129t)$

Table 3. Half-lives in weeks of the added endosulfan and other organochlorine pesticides present in a soil in controlled environments.

Pesticide	Half-life (weeks)			
	Experiments with endosulfan			Experiments without endosulfan (mean of 19-33% water content)
	20% water content	30% water content	Mean	
α -endosulfan	26	45	33	-
β -endosulfan	18	25	22	-
Aldrin	42	56	47	49
Dieldrin	42	73	54	37

Figure 1. Degradation of α - and β -endosulfan in soil at a constant temperature 30°C and two water contents of 20% and 30%.

Figure 2. Degradation of aldrin and dieldrin in an endosulfan labelled soil at two water contents of 20% and 30%.

Figure 3. Degradation of α - and β -endosulfan in a submerged soil at 30°C.

Figure 4. Degradation of dieldrin in two growth chamber experiments, with and without endosulfan, at the constant temperature of 30°C (mean of two water contents of 20% and 30%).