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Stimulation of Aldrin and Dieldrin Loss from Soils Treated with Carbon Amendments and Saturated-Ring Analogues

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Aldrin and its epoxide, dieldrin are organochlorine insecticides long recognized for their environmental persistence, bioaccumulation and toxicity to non-target organisms. Attempts to biodegrade these insecticides using microorganisms have yielded only minor changes to the non-chlorinated ring (Matsumura and Boush, 1967 and 1968; Tu *et al.*, 1968; Patil *et al.*, 1970; Klein *et al.*, 1973; Singh, 1981) and in one study, monodechlorination (Maule *et al.*, 1987).

The use of amendments (such as organic supplements and pesticide analogues) to enhance the biodegradation of organochlorines has received little attention. Maule *et al.* (1987) noted increased monodechlorination of dieldrin in the presence of formate and Guenzi and Beard (1968) found the addition of 1% alfalfa to DDT-contaminated soils promoted the formation of DDD. The present study investigates the effect of carbon amendments and analogues on the disappearance of aldrin and dieldrin residues from soil.

MATERIALS AND METHODS

Soil samples were collected from a 40 m^3 soil pile contaminated with aldrin (6.5 mg kg^{-1}) and dieldrin (3.3 mg kg^{-1}). The samples were sieved through a 5 mm mesh and stored in glass jars at ambient temperatures until used. The soil pile was located at a site in the Beaudesert Industrial estate, Brisbane and was the result of excavations from around the base of 28 wooden power poles treated with a technical aldrin-creosote mix to control termite pests.

Disposable 5 ml syringes were used as incubation vessels for soil samples. They were adapted by cutting the

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injection tip off the syringe. The plunger was then drawn back to maximum capacity and the syringe inverted to provide an incubation chamber for the soil. Ten different soil treatments were used ; one control (no amendments), 4 carbon amendments and 5 pesticide analogues. The carbon amendments used were casamino acids, glucose, xylose and i-inositol. They were added to the soil to give a final concentration of 100 μg g^{-1} dry soil. The pesticide analogues used were cyclohexylchloride [CHC], *trans*-1,2 dichloro-cyclohexane [DCCH], *cis*-decahydronaphthalene (decalin), borneol and isoborneol and these were added to give a final concentration of 10 μg g^{-1} dry soil.

Aldrin-treated soil was weighed into the adapted syringes (3.00 ± 0.05 g per syringe) and moistened with 2 ml of distilled water containing a carbon amendment or no addition at all. Analogues were added as concentrated solutions (50 μl) in a volatile solvent carrier (diethyl ether), since all were water insoluble. Fifteen replicates of each treatment were prepared. Of these, 5 were extracted immediately as zero time controls, 5 were incubated at 28°C for 15 days and 5 were incubated at 28°C for 60 days. All samples were extracted following incubation.

The syringes were incubated, standing upright, in styrofoam trays and covered loosely with plastic sheets to reduce evaporation. The 60 day samples were rehydrated with distilled water during incubation to compensate for evaporation.

Each soil sample was extracted into 3 x 2 ml of nanograde acetone with 5 min mixing on a Rotorack 96 (Fisher Scientific Co., U.S.A.) at 50 rev min^{-1}, between solvent additions. The samples were left to stand for 30 min and then further extracted for 10 min into 5 ml nanograde n-hexane. A 2% Na_2SO_4 solution was added (6 ml) to aid in phase separation. When the phases had separated after 30 min standing, the hexane layer was removed and dried over anhydrous Na_2SO_4.

Extracts were diluted up to 100 fold and analysed on a gas chromatograph (model GC-R1A, Shimadzu, Japan) equipped with a ^{63}Ni electron capture detector and data processor (model RPR-G1). A 2.1 m x 2.6 mm glass column, packed with Gas Chrom Q of 80/100 mesh coated with 1.5% Silicone OV 17 and 1.95% QF 1, was used. The column and detector were operated at 200 and 250°C respectively and an oxygen-free nitrogen carrier gas was used at a flow rate of 50 ml min^{-1}. Aldrin and dieldrin concentrations were computed by the data processor with reference to standard curves for the insecticides.

RESULTS AND DISCUSSION

Soil samples supplemented with xylose and i-inositol showed a marked decrease in detectable concentrations of aldrin (84%-96%) and dieldrin (50%-79%), after 60 days, relative to untreated and zero time controls. Decalin, borneol and isoborneol treated soils produced a statistically significant decrease in aldrin concentration (27%-74%) in the same period of time relative to zero time controls and untreated soil controls. The remaining amendments had no appreciable effect on the levels of insecticide residues in the soil (Table 1). Note that the standard errors were generally large and most likely associated with the heterogeneous nature of the soil samples.

Biodegradation of aldrin and dieldrin in the test soil appears to be stimulated by the addition of xylose and i-inositol. These amendments may be acting as growth substrates for the cometabolism of aldrin and dieldrin by members of the soil microflora. Growth substrates are hypothesised to provide cofactors or metabolites necessary for the catalytic activity of enzymes (usually non-specific) capable of transforming xenobiotics (Janke and Fritsche, 1985).

Although no gas chromatographic evidence is available, initial modifications to the insecticides may have led to sequential degradation of the metabolites by other members of the soil microflora until complete mineralization was achieved. This would explain why aldrin and dieldrin concentrations decreased without the concommitant accumulation of detectable metabolites.

The saturated-ring analogues; decalin, borneol and isoborneol, may have induced one or more enzyme systems capable of transforming aldrin, whereas the chlorinated analogues, which bear only a slight structural resemblance to the insecticides, did not produce a similar effect.

Monodechlorination of dieldrin had already been achieved by Maule *et al.* (1987), but in a highly complex growth medium, containing a variety of trace elements and vitamin supplements. Hence, use of the dechlorination capability in a practical situation would not be possible, eg. *in situ* cleanup of soil.

Practical application of these results to the *in situ* decontamination of aldrin-treated soil, would require that the carbon amendment be cheap and readily available instead of purified and therefore, expensive (as is the case with xylose and inositol). However, with closely related substrates producing conflicting effects on

Table 1. Effect of selected amendments on the detectable[a] aldrin and dieldrin concentration in soil over a 60 day incubation period at 28°C

Amendment[b]	Incubation time (days)	Average concentration[c] in soil ($ng\ g^{-1}$)	
		aldrin	dieldrin
none	0	7025 ± 399	3763 ± 362
	15	7348 ± 818	3662 ± 489
	60	7578 ± 2198	3385 ± 1677
casamino acids	0	6495 ± 351	3638 ± 540
	15	7944 ± 1754	3140 ± 588
	60	7490 ± 3303	4236 ± 2836
glucose	0	5735 ± 723	3210 ± 66
	15	6789 ± 1391	4088 ± 1490
	60	4255 ± 4088	2453 ± 1235
inositol	0	6954 ± 2448	3530 ± 518
	15	6085 ± 1846	2952 ± 880
	60	548 ± 175	1156 ± 204
xylose	0	8221 ± 657	4112 ± 305
	15	7684 ± 5085	3378 ± 1916
	60	535 ± 155	1296 ± 386
CHC	0	7659 ± 138	5212 ± 1252
	15	5624 ± 809	3239 ± 448
	60	7041 ± 1360	4571 ± 1260
DCCH	0	7436 ± 177	4834 ± 1786
	15	8852 ± 2670	6420 ± 3159
	60	6314 ± 1796	3636 ± 821
decalin	0	7338 ± 37	4046 ± 671
	15	6127 ± 962	2417 ± 576
	60	3781 ± 1367	2918 ± 628
borneol	0	7485 ± 171	4250 ± 382
	15	7103 ± 2875	3680 ± 1110
	60	3673 ± 1661	633 ± 1289
isoborneol	0	7393 ± 301	4007 ± 38
	15	7450 ± 2240	4040 ± 1860
	60	3630 ± 833	2757 ± 849

a. detected by GC-ECD
b. CHC = cyclohexylchloride
   DCCH = *trans* 1,2 dichloro-cyclohexane
c. averaged from 5 replicates: ± standard error

biodegradation (stimulation / inhibition), the addition of a carbon source comprised of many components may have no biodegradative advantage.

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