SUGARCANE PESTICIDES AND THEIR RESIDUE ANALYSES

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Abstract

Samples of sugarcane from experimental plots and a sample of high test molasses were analysed by the South African Bureau of Standards for residues of a range of pesticides which may be used in the sugar industry. No residues were detected of the following chemicals: ortho-para DDT, dieldrin, endosulfan, mercaptothion, 2,4-D. Only 0,12 ppm aldicarb was detected in immature sugarcane when it was six months old. (The tolerance limit is 0,10 ppm). No residue of this chemical was found in harvestable cane. Small amounts of para-para DDT, EDB and DBCP were detected, but these were all within acceptable tolerance levels.

Introduction

The necessity for using agricultural chemicals is generally accepted. Many of them are quite harmless to human beings, but insecticides and nematicides particularly include many toxic substances, some of which, in concentrated form can be lethal. The possibility of such substances being taken up by treated plants and stored within their tissues cannot be overlooked, and should be considered when marketing any edible crop.

Sugarcane in South Africa and Swaziland is relatively pest-free, and in order to maintain existing biological control, it has been the policy of the Mount Edgecombe Experiment Station to recommend pesticide use only when absolutely necessary. Such necessity does arise, however, and may involve the use of chemicals which have a high mammalian toxicity. It was decided, therefore, to implement residue analyses for all pesticides recommended to the industry.

Listed below are the various insecticides and nematicides recommended, with comments regarding their use, toxicity, and the source of treated material sampled for residue analyses. One herbicide also is included.

Insecticides

DDT (wide spectrum, LD50 113-300 mg/kg)

A government-imposed agricultural ban exists on this persistent insecticide, but it was included for analysis because existing stocks are still being used. It has been used on sugarcane mainly for the control of trash caterpillars (Noctuidae).

For residue analysis a sample of 15-month-old plant cane of variety NCo 376 was taken from an insecticide trial (against cockchafer beetles) in the Natal midlands. The cane had been treated at planting with DDT 50% wettable powder at the rate of 4,5 kg in 230 litres water per hectare applied in the planting furrow. Normally the cane would have been harvested 24 months after planting.

Dieldrin (wide spectrum, LD50 40-87 mg/kg)

Use of this insecticide is restricted to (1) its employment as a pre-planting sett dip in conjunction with a fungicide, when it is used at the rate of 30 ml 18% emulsifiable concentrate to 5 litres water; (2) its use as a soil insecticide at planting, aimed at cockchafer beetles, when 2,25 kg active ingredient are added to 450 litres water and applied in the planting furrows.

For residue analysis a sample of 15-month-old plant cane was taken from the trial mentioned above, where plots had been treated with 3,9 kg 50% wettable powder in 230 litres water per hectare applied in planting furrows.

Endosulfan (Thiodan) (restricted spectrum, LD50 35-110 mg/kg)

The only agricultrual restriction on this poisonous, but non-persistent insecticide is that waste material of treated crops (eg. cane tops) may not be fed directly to livestock. It is recommended for use against *Numicia viridis* Muir and against trash caterpillars, when 1,4 kg active ingredient are applied per hectare, either as a dust or as an emulsifiable concentrate.

For residue analysis a sample was taken of 11-month-old ratoon cane which had been treated eight months previously as part of an insecticide trial against trash caterpillars. Treatment rate was 1,1 kg 50% wettable powder in 230 litres water per hectare. The cane would normally have been harvested about 20 months after treatment.

Mercaptothion (Malathion) (wide spectrum, LD50 1375-2500 mg/kg)

There is no restriction on this non-persistent insecticide, which has been used effectively and repeatedly against *Numicia viridis,* at the rate of 340 g active ingredient per hectare, either as a 5% dust or as an ultra-low-volume emulsifiable concentrate.

For residue analysis a sample was taken of 15-month-old ratoon cane which had been dusted two weeks previously with a 5% dust at the rate of 45 kg per hectare.

Nematicides

EDB (LD 50 146-420 mg/kg)

This is a fumigant which is applied below soil level before planting, at the rate of 100 kg active ingredient per hectare.

For residue analysis a sample was taken at harvest from a 15-month-old nematicide trial, where 101kg a.i. of the chemical had been applied per hectare.

DBCP (LD50 173 mg/kg)

This is another fumigant which is applied below soil level, usually before planting, at the rate of 50 kg active ingredient per hectare.

For residue analysis a sample was taken from the same trial, where the chemical had been used at a rate of 145 kg per hectare.

Aldicarb (Temik) (LD50 0,5-1 mg/kg)

This is an extremely poisonous nematicide, which was recently registered for use on sugarcane. It is applied below soil level at the time of planting.

For residue analysis three samples were taken. One was taken from the trial which involved the nematicides already mentioned, and a further two samples were taken from immature sugarcane of the kind which might be cut for chewing purposes or be eaten fortuitously by straying animals. The age at which cane becomes palatable for chewing depends on the time of year at which it was

Table 1 Pesticide residue analysis on samples of sugarcane and molasses

Type of sample	Identification of sample	Replicate	DDT and dieldrin content (ppm)		
			pp DDT	op DDT	Dieldrin
15-month-old plant cane	DDT 1	first	0,005	< 0,005	—
		second	0,003	< 0,005	—
	DDT 2	first	0,004	< 0,005	—
		second	0,010	< 0,005	
	Dieldrin 1	first	—	—	< 0,005
		second	—	—	< 0,005
	Dieldrin 2	first	—	—	< 0,005
		second	—	—	< 0,005
High test molasses	Dieldrin	first	—	—	< 0,002
		second	—	—	< 0,002
			Endosulfan content (ppm)		
			α Isomer	β Isomer	Endosulfan sulphate
11-month-old ratoon cane	Endosulfan	first	< 0,01	< 0,01	< 0,01
		second	< 0,01	< 0,01	< 0,01
			Mercaptothion content (ppm)		
15-month-old ratoon cane	Mercaptothion	first	< 0,05		
		second	< 0,05		
			Inorganic bromide (ppm bromide)		
15-month-old plant cane	EDB	first	40		
		second	38		
	DBCP	first	50		
		second	62		
			Aldicarb content as aldicarb sulphone (ppm)		
15-month-old plant cane	Aldicarb	first	< 0,02		
		second	< 0,02		
13-month-old plant cane	Aldicarb	first	< 0,06		
		second	< 0,06		
6-month-old plant cane	Aldicarb	first	0,11		
		second	0,12		
High test molasses	Aldicarb	first	< 0,05		
		second	< 0,05		
			2,4-D acid (ppm)		
High test molasses	2,4-D	first	< 0,20		
		second	< 0,20		

planted or ratooned, the locality and the general growth rate for that particular season. Cane analysed was (1) 13-month-old planted in September on the coast, (2) 6-month-old cane planted in August on the coast. In all cases the application rate was 56 kg of 10% granules per hectare.

Herbicides

2,4-D Group (LD50 300-1000 mg/kg)

Chemicals of this group are used against a wide range of annual grasses and broad-leaf weeds. They are not highly toxic, but are included in this paper because analysis results became available when the Experiment Station was asked to investigate their presence in samples of high test molasses. Residues in sugarcane were not investiggated.

Untreated controls were included for comparison with each treated sample. The cane samples were deep-frozen and despatched in heat-insulated containers by express rail service, to the chemical laboratories of the South African Bureau of Standards, Pretoria, where they were analyzed. In addition one sample of high test molasses was analyzed to see whether traces of dieldrin, aldicarb and the herbicide 2,4-D were detectable. Methods of analysis are given in appendix I.

Results

Table 1 shows that apart from samples treated with EDB and DBCP, in which relatively high quantities of inorganic bromide were present, the only other residues detected were pp DDT and aldicarb as the sulphone (0,12 ppm) in the 6-month-old chewable cane.

Results given as less than a certain value mean that this figure is the lowest detectable limit of pesticide that could be determined under the conditions of analysis, and that no pesticide was detectable at this limit.

TABLE 2

Percentage recovery from treated control samples

Sample	Pesticide	Isomer or metabolite	Amount added (ppm)	Percentage recovery
Sugarcane	DDT	pp DDT	0,10	84
		op DDT	0,10	87
Sugarcane	Dieldrin		0,10	88
Sugarcane	Endosulfan	α isomer	0,20	93
		β isomer	0,20	87
		sulphate	0,20	82
Sugarcane	Mercaptothion		6	95
Sugarcane	Inorganic bromide		50	90
15-month cane	Aldicarb	sulphone	1	89
			2	
13-month cane	Aldicarb	sulphone	0,20	92
6-month cane	Aldicarb	sulphone	0,10	101
Molasses	Dieldrin		0,02	94
Molasses	Aldicarb	sulphone	0,20	91
Molasses	2,4-D	acid	0,20	80

The untreated control samples gave no evidence of the presence of any of the relevant pesticides, except in the case of inorganic bromide where 12 parts per million bromide were detected.

Recovery determinations on treated control samples are shown in Table 2.

Discussion

The amounts of inorganic bromide and pp DDT detected are well within tolerance limits, which are 75 and 7 ppm respectively. Inorganic bromide was detected even in the untreated samples, and it has been suggested (Plant Protection Research Institute, Pretoria, correspondence) that its presence may be related to coastal proximity.

The small amount of aldicarb detected in the young chewable cane was just outside the tolerance limit (0,10 ppm) but to a human being such immature cane would not be palatable. Moreover it should be emphasized that before the end products are presented for human consumption, the harvested cane normally undergoes the processes of milling and refining. This would serve further to reduce any residues remaining at harvest, and none was detectable in the high test molasses sample.

It is concluded that the possibility of dangerous pesticide residues being present at harmful levels in cane of 11 months or more is remote.

Acknowledgement

The authors are grateful to the Director General of the South African Bureau of Standards for permission to reproduce the results of the residue analyses.

Appendix I

Methods of Analysis

The sugarcane samples were passed through a green feed chopper and analyses were carried out in duplicate on 100 g or 50 g portions of the samples.

Insecticides

Dieldrin and DDT Each 100 g portion was extracted with a mixture of isopropanol and hexane in a high speed homogenizer. The extract was washed with water to remove the isopropanol and then passed through a silica gel column using hexane as solvent. This eluate contained the DDT isomers.

The dieldrin content was eluted by passing a solution of 5% ethyl ether in hexane through the column. The para-para (pp) and ortho-para (op) DDT and dieldrin contents of the extracts were determined on a gas chromatograph equipped with an electron capture detector.

To determine dieldrin in molasses, part of the sample was diluted with an aliquot of water and the dieldrin extracted, using hexane as above.

Endosulfan Samples were extracted first with acetone and then hexane. The acetone was removed by evaporation, and after further concentration the combined extracts were made up to 10 ml. Five ml of this extract were passed through an

acidic alumina column and the β endosulfan and endosulfan sulphate were eluted using 30% ether in hexane. Five ml of the extract were passed through a deactivated alumina column and α endosulfan was eluted with hexane as solvent. The α β endosulfan and endosulfan sulphate contents were determined on a gas chromatograph using an electron capture detector.

Mercaptothion Each 50 g portion was extracted using acetone as solvent. The acetone was removed by evaporation and the mercaptothion in the water phase was extracted with hexane. The mercaptothion in the hexane extract was determined on a gas chromatograph using a flame photometric detector and a phosphorus filter.

Nematicides

EDB and DBCP The inorganic bromide present in 50 g portions of sugarcane was allowed to react overnight with ethylene oxide in an acidic acetonitrile solution. The inorganic bromide was determined on a gas chromatograph using an electron capture detector.

Aldicarb (Temik) Each 50 g portion was extracted with acetone. The acetone was removed by evaporation and the aqueous residue extracted with chloroform. After removal of the chloroform the residue was disolved in hexane and extracted using acetonitrile. NaCl solution was added to the acetonitrile phase and this was extracted with chloroform. The chloroform was removed by evaporation and the aldicarb oxidized to the sulphone by hydrogen peroxide in an acetic acid medium. After neutralization the sulphone was partitioned from this solution into chloroform. The aldicarb sulphone content was determined on a gas chromatograph equipped with a flame photometric detector and a sulphur filter.

Aldicarb was extracted by means of chloroform from diluted molasses and then determined as described above.

Herbicide

2,4-D in molasses A portion of the sample was hydrolysed with alkali, acidified and then extracted with chloroform. After the chloroform was evaporated the extract was esterified and the total 2,4-D content was determined using a gas chromatograph equipped with an electron capture detector.

Note:

Recovery determinations were carried out concurrently with the analyses by adding known amounts of each of the pesticides to portions of control sugarcane samples, and the molasses sample.