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FINAL REPORT
SRDC PROJECT BS85S
CONSTITUENTS OF NON-SUGAR PRODUCTS
OF SUGARCANE

by

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SUMMARY

Residues of selected pesticides were measured in samples of bagasse, filter mud and molasses from six sugar mills, in samples of dunder from two distilleries, and in cane tops and soil from four canegrowing areas of Queensland. Where possible, pesticide residue identities were confirmed using GC-MS.

The largest residue concentrations occurred in the bagasse samples; a not unexpected result as limited studies have shown that most of a pesticide residue in sugarcane at harvest remains in bagasse in the milling process. Pesticides detected in bagasse were atrazine, BHC, chlorpyrifos, dieldrin and heptachlor epoxide.

Smaller pesticide residues were detected in some samples of filter mud, molasses, dunder and cane tops. Pesticides detected included BHC, chlorpyrifos, 2,4-D, dieldrin and heptachlor epoxide.

In all cases, the concentration of residues was below the maximum residue set for whole cane.

During the project a multiresidue analytical method was developed for the analysis of selected pesticides in the various non-sugar products of sugarcane.

The low concentrations of pesticides detected do not appear to have the potential to increase environmental degradation where the by-products are returned to the soil. Such return normally occurs in canefields and any pesticide residues present are in the lower range of concentrations already present in these soils.

The sugar industry needs to be more aware of the presence and magnitude of pesticide residues in by-products from sugar mills and distilleries, and in sugarcane in the field, especially as these materials can be used in food production for human consumption.

In view of these implications, it is proposed that:

- pesticide residues in cane tops, both internal and in surface dust adhering to leaves, are determined in a broad, detailed survey yielding sufficient data to fully evaluate the situation;
- the fate of selected pesticides in the milling process is determined using laboratory simulations. This is necessary as there is little information on the distribution of pesticide residues in the milling process.



1.0 INTRODUCTION

Non-sugar products are already used in ways which could result in pesticide residues, if present, entering food for human consumption or being introduced into the environment. Bagasse can be used as a mulch, as a soil improver or can be composted with other materials such as filter mud and used for growing small crops. Some uses are sporadic, such as feeding cane tops to cattle in times of drought. Some products present disposal problems, for example filter mud and dunder; however, these products have fertiliser value and can be returned to the soil. In addition, there is always the possibility of new uses for the products being found where a knowledge of their pesticide residue content could also be important.

Little information is available on pesticide residues in non-sugar products. In the early 1970s, BSES studied the fate of BHC isomers and dieldrin in the raw sugar milling process. This involved the analysis of bagasse, juice, filter mud, molasses, syrup and raw sugar and the results provide some baseline data for these pesticides. The lack of strategic information about pesticide residues caused difficulties in recent droughts when farmers wished to feed cane tops to cattle. This project benefits the sugar industry by providing data on non-sugar products and enhances the industry's image as a responsible user of pesticides. A knowledge of pesticide residue concentrations in non-sugar products also has commercial benefits, where the products are sold for feed supplements or a manufacturer is developing a new use.

As far as is known, most non-sugar products are not analysed to any extent for pesticide residues and it appears that not much attention has been paid to the possible presence of pesticide residues in these products. Pesticide residues could enter food for human-consumption via stock feed or where soil amended with non-sugar products is used for crop production. Pesticide residues could also be released into the environment where products are returned to the soil.

Measurement of selected pesticide residues in non-sugar products allows the potential risks and the need for further research or monitoring to be assessed.

2.0 OBJECTIVES

- Survey pesticide residues in cane leaves, bagasse, filter mud, molasses and dunder.
- Assess the risks to food production and the environment if any significant pesticide residues are found.

3.0 TECHNICAL INFORMATION

There is very little information available on pesticide residue concentrations in non-sugar products. Non-sugar products can be used in food production or returned to the field, so that any pesticide residues present could enter the food chain or the environment.

Annual production of molasses exceeds 700 000 tonnes and almost one-third is fermented for industrial and potable alcohol. The remainder is divided equally between stockfeed and export. Filter mud is spread on canefields. Bagasse is burnt, composted or used as a mulch. Dunder is disposed of by spraying over land. Cane tops and even whole crops are fed to cattle, especially in times of drought; problems arose in certain areas in 1991 where the 'cane hay' sold for stockfeed contained dieldrin residues at the maximum residue limit (MRL).

The sugar industry should be aware of any pesticide residues in non-sugar products, particularly in view of the new environmental and contaminated land legislation in Queensland. This strategic information will be useful when assessing potential new uses for cane by-products. This project underlines the industry's responsible approach to pesticide usage.

4.0 MATERIALS AND METHODS

4.1 Samples

It was decided to sample bagasse, filter mud, molasses, dunder, cane tops and associated soils from sugar mills and distilleries covering a range of canegrowing areas.

Samples of bagasse, filter mud and molasses were obtained from six Queensland sugar mills. Dunder samples were obtained from two distilleries in Queensland. Cane tops and associated soils were obtained from cane farms near Experiment Stations as it was necessary to homogenise the tops in a cutter-grinder for freezing prior to despatch to Brisbane for analysis to meet quarantine requirements for the movement of cane between districts.

4.2 Sampling program

Duplicate samples of bagasse, filter mud and molasses from sugar mills were collected at the beginning, middle and end of the 1992 crushing season. The samples were eight-hour composites, taken at random. Duplicate dunder samples were collected during the same period.

Samples of cane tops and associated soils were collected during the first half of 1993 in the Bundaberg, Mackay, Tully and Burdekin districts.

Samples of cane tops (cabbage and leaf) were homogenised using a cutter-grinder and frozen prior to despatch to Brisbane. All samples were stored frozen at -20°C prior to analysis except for molasses which was stored at room temperature.

4.3 Pesticides

The pesticides investigated were selected from the range currently monitored in raw sugar; BHC isomers, dieldrin, heptachlor and heptachlor epoxide, chlorpyrifos, ametryn, atrazine, 2,4-D, 2,4,5-T, diuron and trifluralin.

4.4 Analytical method development

The analytical methods developed for this project are based on published multiresidue methods (see reference list in Appendix A), adapted to suit the sugar industry samples. The methods were evaluated using recovery studies and test blanks were carried out to determine any possible interferences. Cleanup of sample extracts was achieved using solvent partitioning and solid-phase methods. Routine analysis of check samples containing known amounts of pesticides was carried out to monitor equipment and method performance.

4.5 Extraction scheme

The pesticides selected for investigation were placed into three groups for sample extraction:

- Group 1: BHC isomers, dieldrin, heptachlor, heptachlor epoxide, atrazine, chlorpyrifos and trifluralin
- Group 2: ametryn and diuron
- Group 3: 2,4-D and 2,4,5-T

The samples were extracted with acetone or acetone and methanol mixtures using Soxhlet, reflux or liquid-liquid extraction techniques. After extraction, group 1 pesticides were partitioned into hexane, group 2 into methylene chloride and group 3 into hexane after methylation using acidified methanol. Thus the 140 samples received yielded some 420 extracts for analysis.

4.6 Analysis

The sample extracts were analysed by gas chromatography and high performance liquid chromatography, using electron capture, nitrogen-phosphorus (thermionic specific) and ultra-violet detectors.

The final extracts analysed represented concentration factors, with respect to the original samples, ranging from 2 to 20. This yielded limits of detection in the samples for most of the pesticides analysed ranging from 0.001 to 0.05 mg/kg on a wet-weight basis.

Residue identities were confirmed by gas chromatography-mass spectrometry (GC-MS) in the Agricultural Research Laboratories of the Queensland Department of Primary Industries under a contract arrangement.

5.0 RESULTS

The results are set out below. Detailed results are not presented as only residues of a few chemicals were detected in a small proportion of the samples analysed. Residue concentrations are given for each sample type in terms of mg/kg on a wet weight basis.

5.1 Bagasse

Of the 30 bagasse samples analysed, six contained pesticide residues which were mostly near the limit of detection for the analytical methods used (0.01 to 0.02 mg/kg in bagasse). Residue identities were confirmed using GC-MS.

Chlorpyrifos was detected in four of these samples at concentrations of 0.02, 0.06, 0.10 and 0.11 mg/kg. Atrazine was detected in two of the samples, both 0.07 mg/kg, and atrazine residues were possibly present in a further two samples but at very much lower concentrations. Residues of dieldrin and heptachlor epoxide were also detected in six and four of the samples, respectively, at concentrations of about 0.02 mg/kg. Trace amounts of BHC were possibly present in some samples but these could not be confirmed by GC-MS. Residues of ametryn, diuron, 2,4-D, 2,4,5-T, trifluralin and heptachlor were not detected in any of the bagasse samples.

5.2 Filter mud

Of the 30 filter mud samples analysed, 19 appeared to contain pesticide residues which included BHC, dieldrin, heptachlor epoxide and chlorpyrifos.

A trace amount of heptachlor epoxide, 0.009 mg/kg, appeared to be present in one filter mud sample but it was not possible to confirm this at such a low concentration. Two samples appeared to contain traces of BHC but again the concentrations were too low for GC-MS confirmation. Low concentrations of dieldrin were measured in three samples, two at 0.04 mg/kg and one 0.09 mg/kg, which were confirmed by GC-MS.

The pesticide found most frequently in the filter mud samples was chlorpyrifos. This insecticide was present in some samples from each of the six mill areas. The total number of positive results was 12, from the 30 mud samples analysed, with a concentration range of 0.006 to 0.070 mg/kg. These residues were confirmed by GC-MS.

No residues of ametryn, atrazine, diuron, heptachlor, 2,4,5-T or trifluralin were detected in any filter mud sample. One sample possibly contained a trace of 2,4-D but this could not be confirmed.

5.3 Molasses

Of the 33 molasses samples analysed, only four contained detectable pesticide residues. Two appeared to contain traces of dieldrin, less than 0.005 mg/kg, but it was not possible to confirm the identity of these residues in these samples at such low concentrations using GC-MS.

Another of the four samples appeared to contain chlorpyrifos, 0.001 mg/kg, but this was not confirmed by GC-MS.

Two of the samples contained residues of 2,4-D at 0.02 and 0.05 mg/kg, both of which were confirmed by GC-MS.

No residues of ametryn, atrazine, diuron, heptachlor, heptachlor epoxide, BHC, 2,4,5-T or trifluralin were detected in the samples.

5.4 Dunder

Dunder samples were only obtained from two distilleries and of the 12 dunder samples analysed, only four contained detectable pesticide residues.

All four samples contained chlorpyrifos in the range 0.002 to 0.004 mg/kg. These residues were confirmed by GC-MS. One of the samples contained dieldrin, 0.001 mg/kg, which was also confirmed by GC-MS.

5.5 Cane tops

Nine of the cane top samples appeared to contain traces of BHC or dieldrin; however, these residues were too small to allow their confirmation by GC-MS.

No other pesticides were detected in the cane top samples.

5.6 Soils

Any pesticide residues detected in soil samples collected in conjunction with the cane top samples were identified on the basis of gas chromatographic retention times only. Generally the residue concentrations present were too low for confirmation by GC-MS.

Pesticide residues were present in all soil samples analysed. Chlorpyrifos and trifluralin were the most common residues detected. Low concentrations of dieldrin and BHC were present in most soils, with a dieldrin concentration of 0.14 mg/kg and beta-BHC concentration of 1.0 mg/kg measured in one soil sample from Bundaberg. Other residues detected were atrazine (two samples), diuron (two samples) and a trace of heptachlor epoxide in one sample from the Burdekin. No residues of ametryn, heptachlor, 2,4-D or 2,4,5-T appeared to be present in any soil tested.

The ranges of pesticide residues detected in all samples are summarised in Table 1. No residues of ametryn, heptachlor or 2,4,5-T were detected in any sample.

Table 1

Pesticide residues in non-sugar products mg/kg on a wet-weight basis

Product	BHC	Chlorpyrifos	Dieldrin	Heptachlor epoxide	Atrazine	2,4-D
Bagasse 6/30*	Trace (6)**	0.02-0.11(4)	0.02(6)	0.02(4)	Trace (2), 0.07(2)	ND***
Filter mud 19/30	Trace (2)	0.006-0.07(12)	0.04-0.09(3)	0.009(1)	ND	Trace (1)
Molasses 4/33	ND	0.001(4)	<0.005(2)	ND	ND	0.02-0.05(2)
Dunder 4/12	ND	0.002-0.004(4)	0.001(1)	ND	ND	ND
Cane tops 9/16	Trace (9)	ND	Trace (9)	ND	ND	ND
Soil 16/16***	Trace - 1.0(8)	Trace - 0.18(10)	Trace - 0.14(15)	Trace (1)	0.09-0.20(2)	ND

additional soil results: trifluralin trace - 0.05(11) and diuron 0.16(1)

* number of samples with a detectable residue of any pesticide out of the total number of samples analysed.

** number of samples with detectable residues of each pesticide.

*** ND denotes below limit of detection (see 4.6 Analysis).

6.0 DISCUSSION

All chemicals registered for use on sugarcane have a maximum residue limit (MRL) established, based on data from field trials. When a MRL is recommended for a new chemical, it is ratified by the NHMRC and published in 'The MRL Standard'. The MRL is then considered for incorporation into the Food and Drug Regulations of each State or Territory. MRLs for chemicals in sugarcane are set for cane at harvest, based on the residue concentrations in stalks. The MRLs for the pesticides studied in this project are shown in Table 2.

Table 2
MRLs for pesticides in sugarcane, mg/kg

ametryn	0.05
atrazine	0.10
diuron	0.20
2,4-D	5.0
2,4,5-T	0.05
trifluralin	0.05
chlorpyrifos	0.10
BHC	0.005
dieldrin	0.01
heptachlor	0.02
heptachlor epoxide	0.02

The organochlorine insecticides, BHC and dieldrin, are no longer registered for use on sugarcane and the MRLs shown for these two chemicals in Table 2 are 'environmental' MRLs in recognition of the continuing presence of these two persistent compounds in soil.

When a registered chemical is applied to sugarcane and the label instructions and any withholding period are observed, residues of the chemical in the cane stalks at harvest should not exceed the MRL.

Studies with a limited number of pesticides in other countries and by BSES (unpublished report) have shown that over 90% of a pesticide in cane entering the mill remains in the bagasse. A further quantity is removed in filter mud. As bagasse (wet weight) makes up about 30% of the weight of cane entering the mill, residue concentrations in bagasse could be three times greater than in the cane itself.

The first objective of the project was completed within the time available with the determination of pesticide residues in cane tops, bagasse, filter mud, molasses, dunder and soil samples. Of the pesticides included in the survey, no residues of ametryn, heptachlor or 2,4,5-T were detected in any sample and diuron and trifluralin were detected only in soil samples.

The second objective of the project, to assess the risks to food production and the environment of any significant pesticide residues detected, is addressed as the residues measured in each sample type are discussed below.

As expected, the largest residues occurred in bagasse with a range 0.02-0.11 mg/kg, while residues in the other non-soil samples ranged from trace amounts up to 0.07 mg/kg with most being less than 0.01 mg/kg.

Pesticides detected in bagasse were chlorpyrifos, atrazine, dieldrin, BHC and heptachlor epoxide. The chlorpyrifos concentrations measured, 0.02 to 0.11 mg/kg would represent less than 0.04 mg/kg in cane which is below the MRL of 0.10 mg/kg. Similarly for the other pesticides detected in bagasse, ie atrazine, dieldrin, heptachlor epoxide and BHC. Thus the residues detected are within the range expected from normal agricultural practice.

The presence of these pesticide residues in bagasse should present no hazard to food production or the environment where bagasse is used as a mulch, soil conditioner or composted as the residues would continue to decline quickly, especially atrazine and chlorpyrifos. However, some people could be concerned when such composted mixtures are used for food production, especially in 'organically grown' systems. Pesticide residues in bagasse should not be a hazard where bagasse is burnt as fuel or used to make paper or particle board.

The limited information available on the fate of pesticide residues in the milling process indicates that quantities of residues in juice after crushing are removed in the filter mud during clarification. Any soil present in the cane supply would be removed at this stage and this source probably accounts for some of the residues detected.

Pesticides detected in filter mud were chlorpyrifos, dieldrin, BHC, heptachlor epoxide and 2,4-D. Chlorpyrifos was commonly detected, in the range 0.006 to 0.07 mg/kg, with residues of the other pesticides being less than 0.01 mg/kg.

Filter mud is spread on canefields for its fertiliser value and could be composted with other materials, such as bagasse. The residue concentrations measured in filter mud are well within the range measured in canegrowing soils and would present no increased hazard.

Residues present in filter mud, especially when mixed with bagasse and used for food production, could be seen as a problem in organic growing systems as mentioned in discussion on bagasse residues.

Only dieldrin, chlorpyrifos, at concentrations of less than 0.005 mg/kg, and 2,4-D residues (0.02 and 0.05 mg/kg) were detected in the molasses samples. Molasses is exported, fermented in distilleries and used as fertiliser and stockfeed.

The very low pesticide concentrations would not present a hazard where molasses is used as a fertiliser, as they are in the lower end of the range already present in the soil. Where molasses is used as a stockfeed, a beast consuming two to three kilograms of molasses a day, would have a daily intake of only 2 to 3 μg of chlorpyrifos. This could be insignificant as it has been calculated that for a lactating cow ingesting about 6 μg of dieldrin per day in water, the dieldrin ingested would only contribute one tenth of the MRL for dieldrin in milk butterfat.

The significance of pesticide residues in molasses used for fermentation to produce potable liquor has presumably been investigated by the alcohol industry.

Dunder is the material left after the distillation of fermented molasses in rum or ethanol production. It has some fertiliser value and the very low pesticide residue concentrations in dunder (less than 0.005 mg/kg) would present no hazard in the soil.

The only pesticide residues detected in cane tops were traces of dieldrin and BHC. These residues may not have originated from root uptake but could have been present in soil dust adhering to the leaves as residues have been shown to be transported by this mechanism, particularly in dry periods (BSES unpublished report).

Pesticide residues were present in all soil samples corresponding to the cane tops and, in addition to BHC and dieldrin, residues of atrazine, chlorpyrifos, diuron, heptachlor epoxide and trifluralin were detected. The absence of detectable pesticide residues other than BHC and dieldrin in cane tops is not surprising as many are not persistent or readily translocated in plants.

The distribution and magnitude of the pesticide residues detected in the samples from sugar mills are consistent with the limited information available on the behaviour of pesticide residues in the milling process.

7.0 IMPLICATIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The establishment of a MRL for a pesticide indicates that there is potential for the pesticide to be present in sugarcane in the field. As the MRL is based on the pesticide residue content of the sugarcane stalk at harvest, it does not indicate what residues might be present in cane tops and leaves. Such residues could be significant, especially when pesticides which accumulate in leaves and not in the stalk are used. This could have implications where cane tops or whole crops are fed to livestock in times of drought, as MRLs do not provide a guide to possible residue concentrations in this situation.

Research with a limited number of pesticides reported in the literature has shown that 90% or more of a pesticide residue in sugarcane remains in bagasse in the milling process, with a further amount being removed in filter mud. Thus pesticide residue concentrations, on a wet-weight basis, can increase three-fold from sugarcane stalks to bagasse. This could have implications in situations where bagasse, as a mulch or soil conditioner, or in composted mixtures with filter mud, is used for growing food crops.

The difficulties with this type of research include:

- the sensitive nature of the investigation. Many mills are not willing to be involved and have concerns about the dissemination of the results. Much time was lost at the beginning of this project in negotiations with mills for their participation;

- the lengthy nature of the analyses, particularly working often at the limit of analytical detection. Also the need for residue identity determination using GC-MS. These factors severely limit the number of samples that can be analysed in given period.

In view of the implications of the results of this project, it is proposed that future research is undertaken:

- to determine pesticide residues in cane tops, both internal and in dust adhering to the leaves. This should be a broad, detailed survey yielding sufficient data to fully evaluate the situation;
- to determine the fate of selected pesticides in the milling process using laboratory simulations. This is necessary as there is little information on the distribution of pesticide residues in mill by-products.

8.0 PUBLICATIONS

Due to the sensitive nature of this area of research, none of the material reported here has been published. There are unlikely to be any publications arising out of this project in the near future, at least.

9.0 ACKNOWLEDGEMENTS

The agreement to supply samples for analysis by the management of six sugar mills and two distilleries is gratefully acknowledged, as is the assistance of the mill staff who collected the samples.

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APPENDIX A

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