

## STUDIES OF ARSENIC SPRAY RESIDUES ON APPLES

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### SUMMARY.

During the 1954-55 and 1955-56 seasons two trials were carried out in the Stanthorpe district to obtain data on arsenic spray residues on apples.

It is evident from these trials that lead arsenate is not weathered appreciably from the fruit, and during the season the gradual reduction in arsenic residue as p.p.m.  $As_2O_3$  is largely the result of fruit growth. One 3 lb./100 gal. spray applied to the variety Granny Smith at a dosage rate of  $1\frac{1}{4}$  gal. per tree in late November resulted in residues of less than 0.6 p.p.m. at early harvest in early January, and at the same dosage rate and timings the mean residue from a double strength spray was 1.46 p.p.m.

### I. INTRODUCTION.

In the Stanthorpe district lead arsenate sprays were used for many years in the control of apple pests. Recently, however, an arsenic residue problem has been given some prominence. Although satisfactory alternative sprays are now available for most of the common pests (May and Bengtson 1955), there is a tendency to continue using the old insecticide. The two trials reported in this paper were carried out to obtain data on arsenic spray residues on apples under conditions prevailing in the Stanthorpe district.

In Queensland, the current tolerance limit for arsenic as  $As_2O_3$  is 1.4 p.p.m.

### II. MATERIALS.

The following materials were used:—

*Lead arsenate*.—A powder containing 31 per cent.  $As_2O_3$  as lead arsenate, and 1 per cent. dispersing agent: containing less than 0.5 per cent. water-soluble arsenic compounds.

*DDT*.—An emulsion concentrate containing 25 per cent. *p,p'* isomer w/v.

*Parathion (E605)*.—An emulsifiable preparation containing 50 per cent. w/v active ingredient.

### III. METHODS.

The trials were set out, during the 1954-55 and 1955-56 seasons, as randomised blocks with a single tree of the variety Granny Smith as the plot unit.

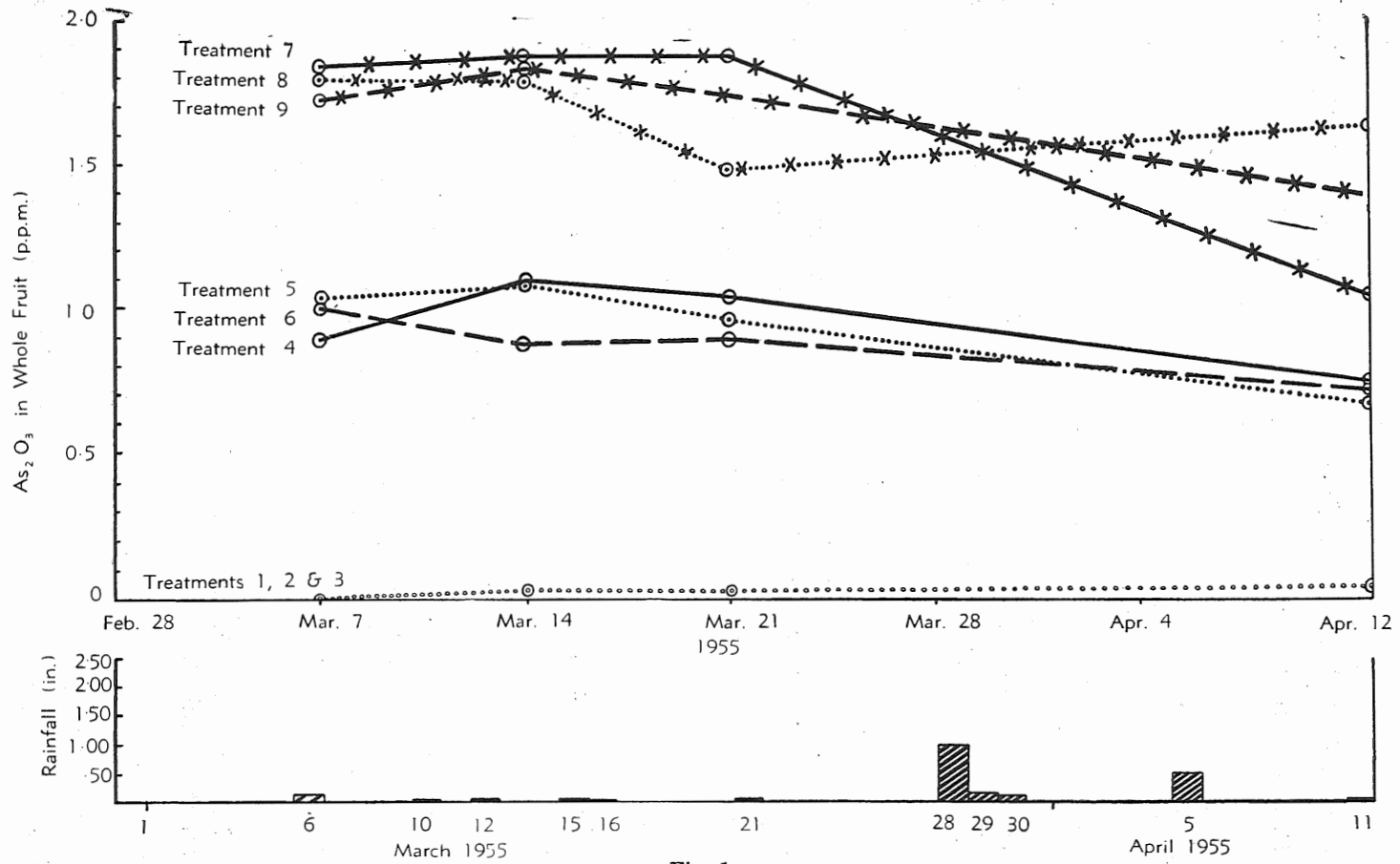


Fig. 1.

Arsenic Residues in Whole Fruit, 1954-55 Season.

Treatment sprays, details of which are given with the results, were formulated with due regard to spray combinations which may be used commercially. These were applied at the rates of  $1\frac{1}{2}$  gal. per tree in the first trial and  $1\frac{1}{4}$  gal. per tree in the second, using a small power unit at nozzle pressures of 250 lb. and 200 lb. per sq. in. All programme sprays not containing lead arsenate (May and Bengtson 1955) were applied prior to both trials, and also during the 1955-56 trial, which occupied the greater part of the season.

Samples of 10 fruit were taken at random intervals from each plot. The fruit was picked into a commercial picking bag, and then placed in a brown paper bag for despatch to the laboratory. As far as possible the method of handling fruit was constant.

In the laboratory each sample was weighed before being thinly peeled. The peeled fruit was then weighed, and the difference between the weights was taken as the weight of peel.

Each peel sample was placed in a 600 ml. beaker, and 100 ml. of concentrated nitric acid was added. The beaker was covered with a watch-glass and heated on a water-bath until a homogeneous mixture with little or no stringiness resulted. After cooling, the contents were transferred to a 500 ml. volumetric flask. An aliquot, usually 25 ml., was digested according to the method of Allcroft and Green (1935) and arsenic as  $As_2O_3$  was determined by a standard Gutzeit method. Representative samples of flesh were treated similarly.

In the statistical analyses the results from treatments not including lead arsenate were excluded, since the residues in such cases were very small or zero. The results from the other treatments were analysed in terms of a logarithmic transform. Treatment averages, in equivalent p.p.m. in peel and whole fruit, are given in Tables 1, 2, 4 and 5; and for whole fruit only are shown graphically with the rainfall records in Figs. 1 and 2.

The product of average fruit size and arsenical residue has been used as a measure of arsenical load per fruit.

Analyses of variance were carried out, using a logarithmic transformation after excluding the zero values.

Further details of each trial are also given with the results.

#### IV. RESULTS.

##### (1) 1954-55 Season.

This trial was a  $9 \times 4$  randomised block and treatments were applied on Feb. 28, 1954. The original intention was to determine DDT residues also but this could not be accomplished with the facilities available.

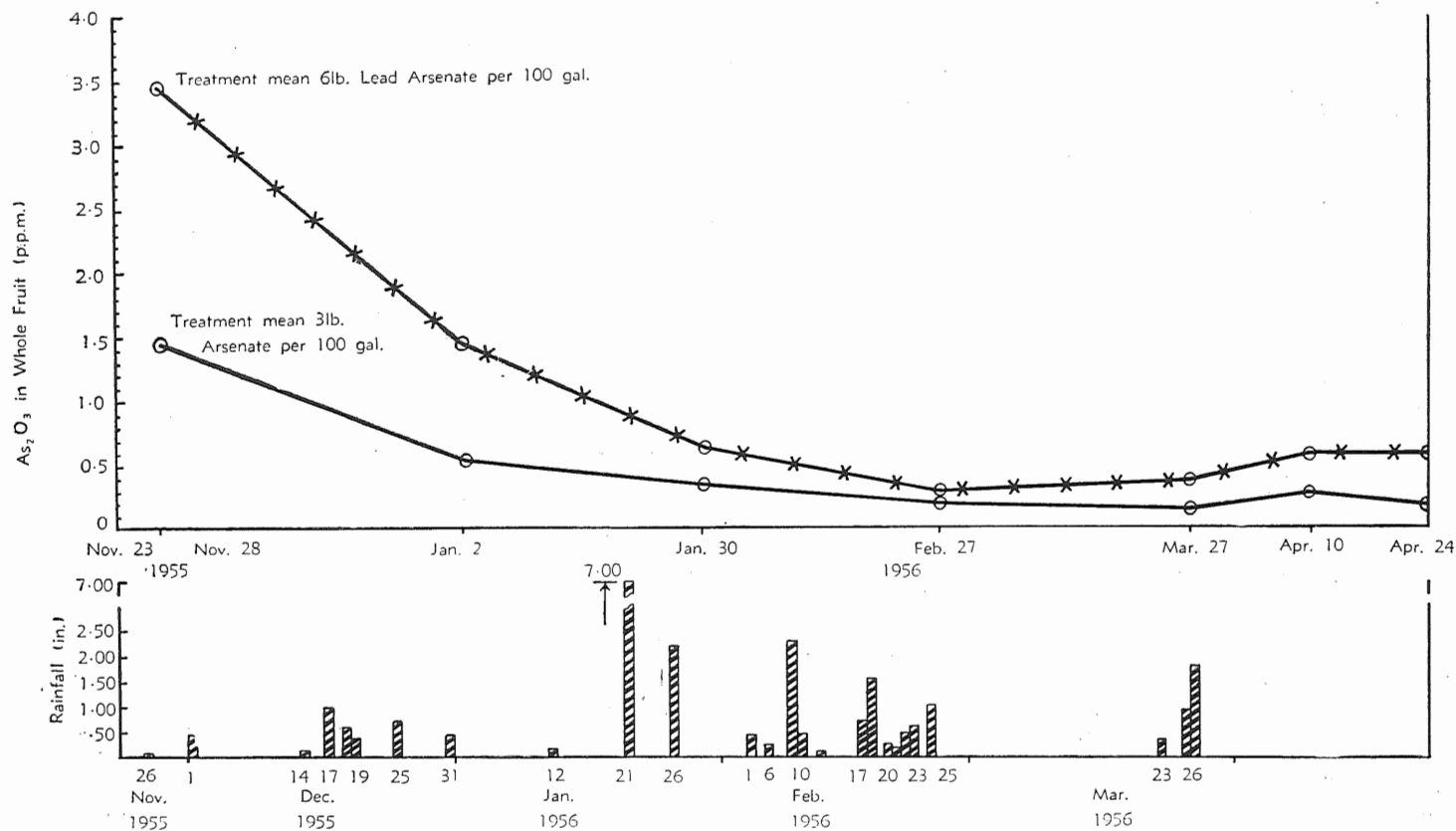


Fig. 2.

Arsenic Residues in Whole Fruit, 1955-56 Season.

Treatments were as follows:—

- (1) Untreated.
- (2) DDT 0.1 per cent.
- (3) DDT 0.2 per cent.
- (4) Lead arsenate 3 lb./100 gal.
- (5) Lead arsenate 3 lb./100 gal. + DDT 0.1 per cent.
- (6) Lead arsenate 3 lb./100 gal. + DDT 0.2 per cent.
- (7) Lead arsenate 6 lb./100 gal.
- (8) Lead arsenate 6 lb./100 gal. + DDT 0.1 per cent.
- (9) Lead arsenate 6 lb./100 gal. + DDT 0.2 per cent.

Strengths of DDT sprays are given as percentages of *p,p'* isomer.

The results appear in Tables 1-3.

**Table 1.**  
AS<sub>2</sub>O<sub>3</sub> IN PEEL (p.p.m.).

Treatment.		Sampling Date.			
DDT	Lead arsenate.	Mar. 7.	Mar. 14.	Mar. 21.	Apr. 12.
0	3 lb./100 gal. .. ..	7.50	9.75	9.84	7.20
0.1%	3 lb./100 gal. .. ..	8.85	9.70	9.01	6.22
0.2%	3 lb./100 gal. .. ..	8.79	8.09	8.53	7.30
	Average .. ..	8.35	9.15	9.11	6.89
0	6 lb./100 gal. .. ..	15.98	16.23	17.23	9.46
0.1%	6 lb./100 gal. .. ..	15.46	16.61	13.85	15.39
0.2%	6 lb./100 gal. .. ..	14.00	16.70	16.92	13.48
	Average .. ..	15.12	16.51	15.92	12.51
Average weight of peel (g.)..		15.8	15.9	16.6	19.9

No arsenic was found in the flesh of the apples.

On all sampling dates the differences between the levels of lead arsenate were highly significant, the residues from the 6 lb./100 gal. spray being about 1.8 times those of the 3 lb./100 gal. application. There is no evidence that the presence of DDT in the spray affected arsenic residues. The arsenic load did not decrease over the period of 36 days.

Forty-three days after applying one 6 lb./100 gal. spray at the rate of 1½ gal. per tree the arsenic residue was only slightly under the allowable 1.4 p.p.m.

**Table 2.**  
As<sub>2</sub>O<sub>3</sub> IN WHOLE FRUIT (p.p.m.).

Treatment.		Sampling Date.			
DDT	Lead arsenate.	Mar. 7.	Mar. 14.	Mar. 21.	Apr. 12.
0	3 lb./100 gal. . . .	.89	1.10	1.05	.75
0.1%	3 lb./100 gal. . . .	1.04	1.09	.97	.68
0.2%	3 lb./100 gal. . . .	1.01	.89	.91	.73
	Average . . . .	.98	1.03	.98	.72
0	6 lb./100 gal. . . .	1.85	1.88	1.88	1.06
0.1%	6 lb./100 gal. . . .	1.80	1.80	1.49	1.63
0.2%	6 lb./100 gal. . . .	1.73	1.84	1.75	1.40
	Average . . . .	1.80	1.84	1.70	1.34
Average weight of fruit (g.)		137.0	143.5	155.5	187.2

**Table 3.**  
AVERAGE ARSENICAL LOAD PER FRUIT ( $\mu$ g.).

Lead arsenate Spray Concentration.	Sampling Date.			
	Mar. 7.	Mar. 14.	Mar. 21.	Apr. 12.
3 lb./100 gal. . . .	134	144	152	135
6 lb./100 gal. . . .	247	273	273	267

**(2) 1955-56 Season.**

This trial was a 6 x 4 randomised block and treatments were applied on Nov. 23 and 24.

Treatments were as follows:

- (1) Untreated.
- (2) Parathion 0.01 per cent. + DDT 0.1 per cent.
- (3) Parathion 0.01 per cent. + DDT 0.1 per cent. + lead arsenate 3 lb./100 gal.
- (4) Parathion 0.01 per cent. + DDT 0.1 per cent. + lead arsenate 6 lb./100 gal.
- (5) Lead arsenate 3 lb./100 gal. followed in 24 hours by parathion 0.01 per cent. + DDT 0.1 per cent.
- (6) Lead arsenate 6 lb./100 gal. followed in 24 hours by parathion 0.01 per cent. + DDT 0.1 per cent.

Strengths of emulsion sprays are given in percentages of active ingredients.

The results are given in Tables 4-6.

**Table 4.**  
As<sub>2</sub>O<sub>3</sub> IN PEEL (p.p.m.).

Sampling Date.	3 lb./100 gal. Treatments.			6 lb./100 gal. Treatments.		
	S*.	A†.	Mean.	S*.	A†.	Mean.
Nov. 28 .. ..	7.36	6.70	7.02	17.18	15.14	16.11
Jan. 2 .. ..	3.53	3.43	3.48	8.67	8.95	8.81
Jan. 30 .. ..	2.82	2.27	2.53	4.67	4.70	4.68
Feb. 27 .. ..	1.29	1.45	1.37	2.33	1.95	2.15
Mar. 27 .. ..	0.79	1.49	1.08	3.70	2.44	3.01
Apr. 10 .. ..	2.08	2.01	2.05	4.59	4.23	4.41
Apr. 24 .. ..	1.45	1.55	1.50	4.56	4.82	4.69

\* S=0.01% parathion and 0.1% DDT applied with the lead arsenate.

† A=0.01% parathion and 0.1% DDT applied 24 hours after the lead arsenate.

**Table 5.**  
As<sub>2</sub>O<sub>3</sub> IN WHOLE FRUIT (p.p.m.).

Sampling Date.	3 lb./100 gal. Treatments.			6 lb./100 gal. Treatments.		
	S*.	A†.	Mean.	S*.	A†.	Mean.
Nov. 28 .. ..	1.48	1.43	1.45	3.50	3.36	3.44
Jan. 2 .. ..	0.55	0.58	0.56	1.44	1.48	1.46
Jan. 30 .. ..	0.40	0.32	0.36	0.65	0.62	0.64
Feb. 27 .. ..	0.19	0.20	0.19	0.33	0.27	0.30
Mar. 27 .. ..	0.11	0.19	0.14	0.46	0.32	0.38
Apr. 10 .. ..	0.30	0.26	0.28	0.62	0.56	0.59
Apr. 24 .. ..	0.18	0.19	0.19	0.59	0.59	0.59

\* S=0.01% parathion and 0.1% DDT applied with the lead arsenate.

† A=0.01% parathion and 0.1% DDT applied 24 hours after the lead arsenate.

**Table 6.**  
AVERAGE ARSENICAL LOAD PER FRUIT (μg.).

Sampling Date.	Lead arsenate Spray Concentration.	
	3 lb./100 gal.	6 lb./100 gal.
Nov. 28 .. ..	57	124
Jan. 2 .. ..	43	111
Jan. 30 .. ..	45	77
Feb. 27 .. ..	30	46
Mar. 27 .. ..	28	75
Apr. 10 .. ..	56	115
Apr. 24 .. ..	38	118

No arsenic was found in the flesh of the apples.

These results are in general similar to those from the earlier trial. Some residue values, however, are distinctly low but these do not detract from the general conclusions: the samples concerned were taken under wet orchard conditions (see Fig. 2).

## V. DISCUSSION.

It is evident from these trials that lead arsenate is not weathered appreciably from the fruit, and during the season the gradual reduction in arsenic residues as p.p.m. is largely due to fruit growth.

In Stanthorpe apple orchards the calyx spray is applied in October, and the spray programme continues with applications in early November (about two weeks after the calyx spray), late November, mid-December, early to mid-January and late January to early February. District harvesting of some cooking varieties may commence in early December, and the variety Granny Smith may be picked as cookers in early January.

Under the conditions of these trials, using the variety Granny Smith, one lead arsenate spray of the recommended commercial strength (3 lb./100 gal.) applied in late November resulted at early harvest time in residues of less than 0.6 p.p.m., and with the same timings the residue from a double-strength spray was 1.46 p.p.m. Fruit growth of the earlier varieties is comparatively rapid, and a corresponding reduction in residues (p.p.m.) would occur before harvesting. Further use of lead arsenate after late November, however, would be dangerous so far as the residue tolerance limit for arsenic is concerned.

May and Bengtson (1955) warned that to avoid undesirable residues lead arsenate should not be used after early November. This allows an increased safety margin for differences which may occur between experimental and commercial arsenic residues.

## VI. ACKNOWLEDGEMENTS.

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