

Methamidophos residues in Capsicum fruit

A report prepared for
**NZ Vegetable and Potato Growers'
Federation Incorporated
Fresh Vegetable Sector**

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October 1999

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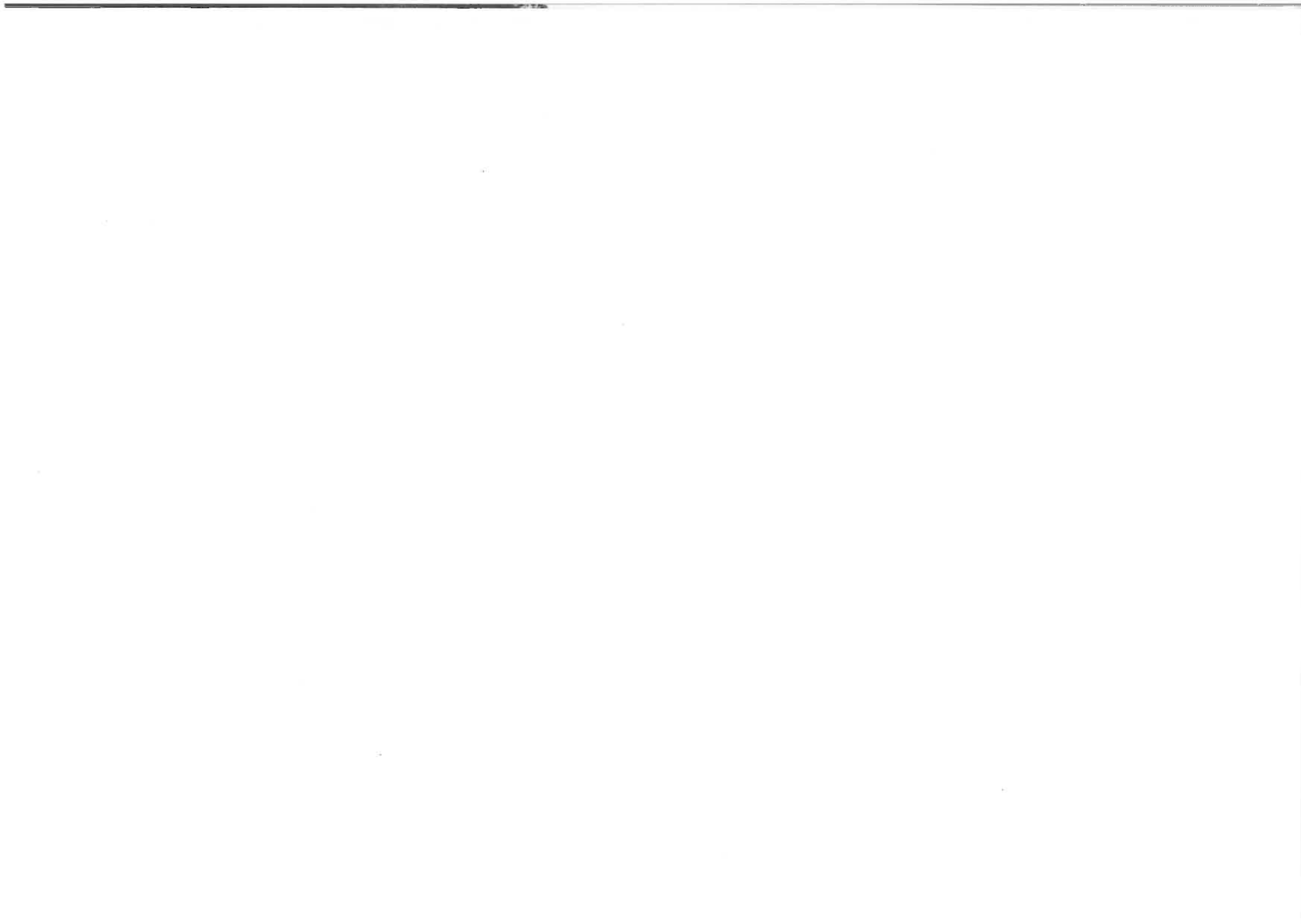
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**Methamidophos residues in
Capsicum**
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1 EXECUTIVE SUMMARY

A major Auckland food retail company (Progressive Enterprises Ltd) recently found unacceptable levels of the pesticide, methamidophos, in capsicum fruit after routine checks. The level of methamidophos was found to be well above the maximum residue limit (MRL), even 28 days after supply of the fresh produce. Concern was expressed to the NZ Vegetable and Potato Growers' Federation Incorporated (Vegfed) Fresh Vegetable Sector. Moreover, there have been reports from growers of the off-label use of the systemic pesticide, methamidophos, at frequent and close spray intervals in capsicum and other greenhouse vegetable crops grown hydroponically. The insecticide has been applied to control aphids and caterpillars. Crop & Food Research was commissioned by Vegfed to investigate methamidophos residues in capsicum fruit as a consequence of its frequent off-label use.

1.1 Experiment to investigate residue levels

An existing trial crop of capsicum in full production was used for the investigation. Methamidophos was applied at the rate of 900 g ai/ha as a soluble concentrate in two separate trials. In one trial, methamidophos was sprayed at 3-day intervals, three times. After the third application, sample fruit were picked when the spray was dry, and again on Days 1, 2, 3, 5, 7, 14, 21 and 28 days after spraying. In another trial, methamidophos was sprayed at the above rate once only, and sample fruit were also picked when the spray was dry, and on Days 1, 2, 3, 5, 7, 14, 21 and 28 after spraying. Fruit was picked from each replicate, bulked and stored at -20°C until all the sampling was completed. Frozen fruit were transported to Analytical Research Laboratories in Napier where methamidophos residues were quantified in the fruit samples.

The maximum residue limit (MRL) for methamidophos, as prescribed in the NZ Food Standard 1999 is set at 0.2 mg/kg for fruiting vegetables. In the first trial, fruit picked from plants that had been sprayed three times at 3-day intervals were found unsafe for consumption up to 2 days following the third spray application. Frequent and close spray intervals application did not have an additive or compounding effect on the decay of methamidophos residues in the capsicum fruit. When plants were sprayed only once with methamidophos, residues in fruit were at unacceptable levels for about the same period after spraying. In both of the trials, fruit was safe for consumption 3 days after pesticide application.

1.2 Conclusions and recommendations

Based on our findings in these trials, it is unlikely that methamidophos residues on capsicum fruit will exceed the MRL about 3 days after conventional pesticide application. In our experiment this was true even if the pesticide was applied at frequent and close intervals.

Our study suggested that the unacceptable methamidophos levels detected in capsicum fruit by Progressive Enterprises Ltd may be as a result of growers using non-conventional methods of applying pesticide.

The conventional application method and normal route of uptake of this systemic pesticide is foliar. However, with more growers turning to hydroponics to produce capsicum and other greenhouse vegetables, other methods of pesticide application may be used, such as adding pesticide to the hydroponic nutrient solution. There are currently no data for the effect of this off-label pesticide use and application method on the level of residues in fresh produce. A comprehensive investigation should be urgently carried out to gather such data, particularly in hydroponically grown vegetables used for fresh consumption.

2 INTRODUCTION

A major food retail company (Progressive Enterprises Ltd Auckland) recently found unacceptable levels of the pesticide, methamidophos, in capsicum fruit (*Capsicum annuum*) after routine checking. The levels of methamidophos were found to be well above the acceptable maximum residue limits (MRL), even 28 days after supply of the fresh produce. Concern was expressed to the NZ Vegetable and Potato Growers' Federation Incorporated (Vegfed) Fresh Vegetable Sector. Moreover, there have been reports from concerned growers of the off-label use of systemic pesticides like methamidophos at frequent and close spray intervals for the control of aphids and caterpillars in vegetables, particularly capsicums. Crop & Food Research was commissioned by Vegfed's Fresh Vegetable Sector to investigate methamidophos residues in capsicum resulting from applying the pesticide as a foliar spray.

3 MATERIAL AND METHODS

3.1 Location of trials

The trials (Fig. 1) were carried out in a greenhouse at the Massey University Plant Growth Units located next to Crop & Food Research, Food Industry Science Centre, Palmerston North.



Figure 1: Capsicum plants used for trials

3.2 Design, layout and treatments

Seed of the capsicum cultivar, Belly Boy, was sown in a nursery, and forty capsicum seedlings were transplanted on 15 December 1998 into polythene bags (PB40) containing an amended general purpose potting mix, in a greenhouse with a floor area of 100 m². The crop was irrigated twice daily through an automatic trickle irrigation system. Liquid nutrients were delivered to each bag in the irrigation water. The amount of nutrients supplied to each plant was adjusted depending on the growth stage of the crop. Nutrients were added weekly to allow for uninterrupted feeding and to maintain vigorous plant growth.

Plants in the bags were spaced 0.5 m apart in rows, with 0.8 m between rows. A distance of 1.2 m between every two rows facilitated removal of laterals and fruit picking. Plants were supported with plastic twines tied to wires across the house at a height of 2.5 m. Lateral shoots were removed each week during crop growth to maintain plant vigour. When the plants were about 50 cm tall, two leaders were allowed to grow vertically and topped at 2.2 m to maintain uniformity and encourage sufficient fruiting for the residue trial.

Forty plants in full production were split into two blocks of 20 plants each, to be used in two separate spray trials. The blocks were separated by a 1 m aisle. Four rows of five plants made up each block. A once-only spray treatment in one trial, and a treatment of three sprays at 3-day intervals in another, were laid out in a randomised complete block design with four replicates.

On 1 June, the first application in Trial I of the pesticide Tamaron™ (containing the active ingredient methamidophos at 600 g/L) was sprayed on the fruiting plants at 1.5 L/ha (equivalent to 900 g ai/ha) in 100 L of water. The treatment was applied using a Solo® knapsack sprayer with a pressure gauge fitted, and operating pressures were in the range of 1-1.5 bars (100-150 kPa). The plants, including fruit, were sprayed to incipient run-off. A further two applications were carried out on 4 and 7 June, at 3-day intervals to simulate common grower practice. On 7 June, in Trial II a single application at the same rate was carried out on plants. Each replicate was sprayed separately. Care was taken to minimise spray drift.

3.3 Sampling, transport and analysis

In Trial I, before the second and third spray applications, fruit samples were taken followed by a sample when the spray had dried, and again on Days 1, 2, 3, 5, 7, 14 and 28 following application.

In Trial II, where the capsicum plants were sprayed once, fruit was also sampled as soon as the spray had dried, and on Days 1, 2, 3, 5, 7, 14 and 28 days after spraying (Table 1). A pre-application sample was also taken.

Care was taken to sample marketable sized fruit only. One capsicum fruit was sampled from each replicate and placed in a plastic bag. A bulked sample across four replicates consisted of four capsicum fruit. The samples were then removed to the laboratory, weighed and stored at -20°C until all samples had been taken. Frozen capsicum samples were transported by Tranzlink Refrigerated to Analytical Research Laboratories (ARL) in Napier for laboratory analysis of methamidophos residues. The capsicum fruit was bulked for analysis.

Table 1: Sampling schedules for methamidophos residues in capsicums in Trials I & II

Trial I: Treatment - three sprays at 3-day intervals		
Day and date sampled	Days after spraying	Comments
Tue 1-6-99	0	1 st spray application (pm)
Wed 2-6-99	1	No sample taken
Thu 3-6-99	2	No sample taken
Fri 4-6-99	0	Pre 2 nd spray sample followed by 2 nd spray
Sat 5-6-99	1	No sample taken
Sun 6-6-99	2	No sample taken
Mon 7-6-99	3	Pre 3 rd spray sample followed by 3 rd spray
Mon 7-6-99	0	Day 0 (when spray fully dry)
Tues 8-6-99	1	Day 1 sample
Wed 9-6-99	2	Day 2 sample
Thu 10-6-99	3	Day 3 sample
Sat 12-6-99	5	Day 5 sample
Mon 14-6-99	7	Day 7 sample
Mon 21-6-99	14	Day 14 sample
Wed 28-6-99	28	Day 28 sample

Trial II: Treatment - one spray application only		
Day and date sampled	Days after spraying	Comments
Mon 7-6-99	0	Pre-spray sample
Mon 7-6-99	0	Day 0 (when spray fully dry)
Tues 8-6-99	1	Day 1 sample
Wed 9-6-99	2	Day 2 sample
Thu 10-6-99	3	Day 3 sample
Sat 12-6-99	5	Day 5 sample
Mon 14-6-99	7	Day 7 sample
Mon 21-6-99	14	Day 14 sample
Wed 28-6-99	28	Day 28 sample

4 RESULTS

A summary of methamidophos residues in the capsicum samples analysed by ARL (Appendix I) is presented in Figs. 2 and 3.

Methamidophos residues found in capsicum fruit in the compounded three spray applications, 3-days apart, initially showed high levels immediately after spraying. Pesticide residues gradually reduced to about 0.09 mg/kg by the third day after the final application of the pesticide (Fig. 2) and reduced further (by 33%) from the

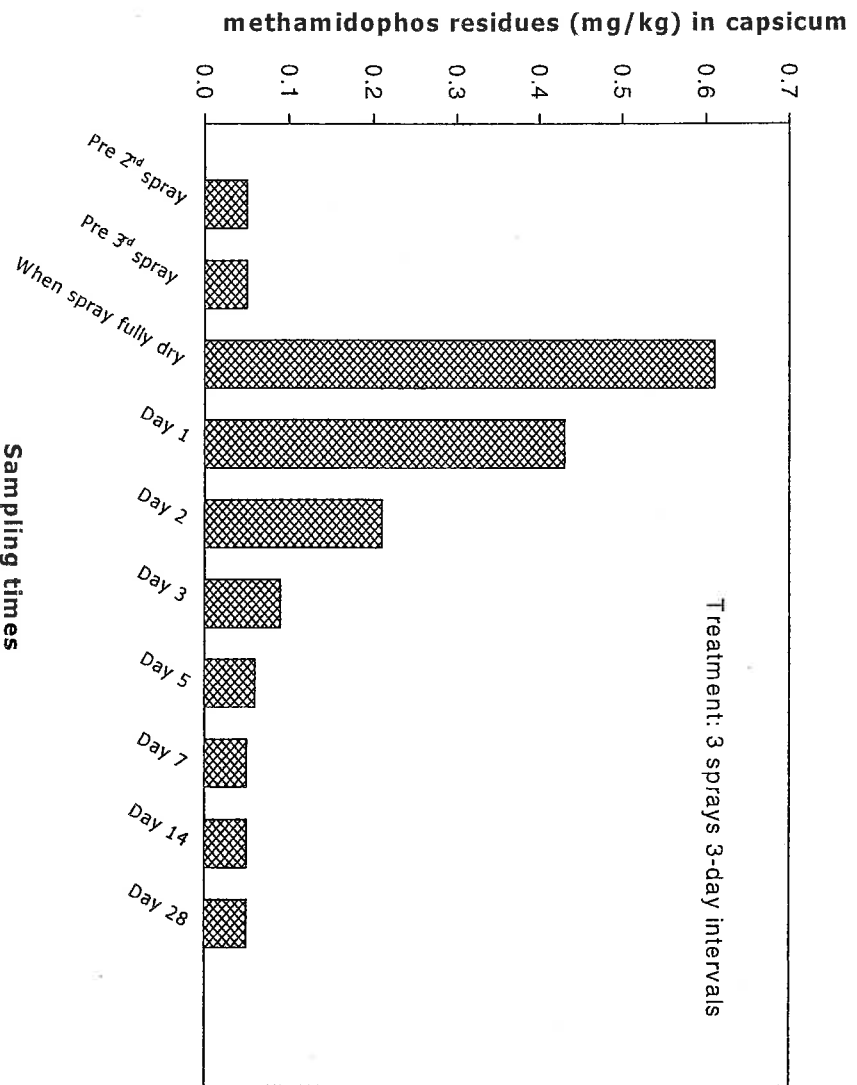


Figure 2: Methamidophos residues found in capsicum from Trial I (three applications at 3-day intervals). Data are from the analysis from bulked capsicum fruit from four replicates.

previous level by about 5 days after spraying. Methamidophos residues continued to be detected at 28 days however, but only at trace levels.

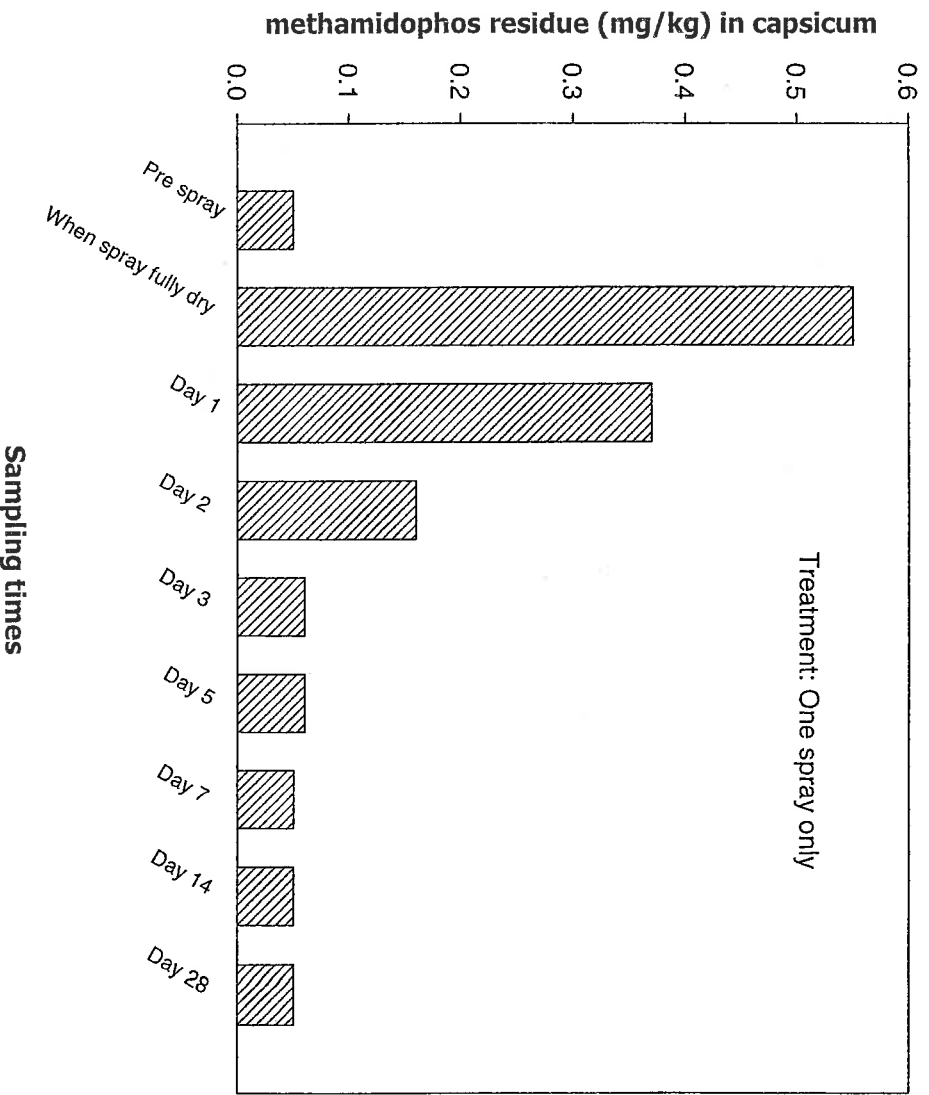


Figure 3: Methamidophos residues found in capsicum from Trial II (single application). Data are from the analysis of bulked capsicum fruit from four replicates.

In Trial II (single spray treatment) (Fig. 3), the trend of methamidophos residues in fruit was similar to that detected in Trial I. The levels were initially high immediately after spraying, but reduced to about 0.02 mg/kg two days after spraying. Residues were detectable 28 days after spraying, but again only at trace levels.

5 DISCUSSION

The maximum residue limit (MRL) for methamidophos prescribed by the NZ Food Standard 1999¹ is 0.2 mg/kg for fruiting vegetables. Capsicum fruit are generally classed as a fruiting vegetable. In the present study, fruit from the crop that was sprayed only once, contained unsafe levels of methamidophos residues for human consumption up to 2 days after spraying. After this period the levels were found to be below the MRL. Surprisingly, when the crop was treated with three applications at 3-day intervals, residues found in fruit showed the same reducing trend. Fruit was unsafe for consumption up to about 3 days after the third spray application. The frequent spray regime did not have an additive or compounding effect on the decay of methamidophos residues in capsicum fruit. Residue levels 3 days after the third spray were well below the MRL.

On the basis of these findings, it is unlikely that methamidophos residues found in capsicum will be over the MRL about 3 days after the last application, if the pesticide is applied conventionally. In this trial this was the case, even if the pesticide was applied at frequent and close intervals.

Our study suggested that the unacceptable methamidophos levels detected in capsicum fruit by Progressive Enterprises Ltd may be the result of growers using non-conventional methods to apply the pesticide.

The conventional application method and normal route of uptake of this systemic pesticide is foliar. However, now that more growers are using hydroponics to produce capsicum and other greenhouse vegetables, other methods of applying the pesticide may be used. These may include incorporating the pesticide in the hydroponic nutrient solution. There are currently no data for this off-label use of the pesticide or its effect on the level of residues in produce. A comprehensive investigation is needed to gather data on the extent of off-label use of pesticides, and the effect of such practices on residues in hydroponic greenhouse vegetables, particularly for fresh consumption.

¹ New Zealand (Maximum Residue Limits of Agricultural Compounds) Food Standard 1999

6 ACKNOWLEDGEMENT

Ray Johnstone, Lesley Taylor and Lyn Sylva are thanked for assistance in plant propagation and general maintenance of the trials described here.

7 APPENDICES

Appendix I: ARL laboratory report

ANALYTICAL RESEARCH LABORATORIES LTD

890 Waitangi Road
 Awatoto, Napier
 PO Box 989, Napier
 New Zealand
 Telephone 06 835 9222
 Facsimile 06 835 9223
 Email: arhb1@xtra.co.nz

Date: 13 September 1999

Lab. #: GC99/4495

Date received: 2 August 1999

Client: Crop & Food Research
 Private Bag 11 030
PALMERSTON NORTH
 Attn: Dr H. Krishna

ANALYSIS: Methamidophos residue

Sample description: Capsicum

*** RESULTS (mg/kg)**

SAMPLE NO.	SAMPLE LABEL	METHAMIDOPHOS
# 1-10 Lot 2		
1	Pre 1 st Spray 7,6,99	<0.05
2	7,6,99 Day 0	0.55
3	8,6,99 Day 1	0.37
4	9,6,99 Day 2	0.16
5	10,6,99 Day 3	0.06
6	12,6,99 Day 5	0.06
7	14,6,99 Day 7	<0.05
8	21,6,99 Day 14	<0.05
9	28,6,99 Day 21	<0.05
10	6,7,99 Day 28	<0.05

* Expressed on samples as received and includes a correction for the recovery.

cntd



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Lab No.: GC99/4495

RESULTS cntd (mg/kg)

SAMPLE NO.	SAMPLE LABEL	METHAMIDOPHOS
# 11-21 Lot 1		
11	Pre 2 nd Spray 4.6.99	<0.05
12	Pre 3 rd Spray 7.6.99	<0.05
13	7.6.99 Day 0	0.61
14	8.6.99 Day 1	0.43
15	9.6.99 Day 2	0.21
16	10.6.99 Day 3	0.09
17	12.6.99 Day 5	0.06
18	14.6.99 Day 7	<0.05
19	21.6.99 Day 14	<0.05
20	28.6.99 Day 21	<0.05
21	6.7.99 Day 28	<0.05

*Expressed on samples as received and includes a correction for the recovery.

Recovery:

Added (mg/kg) Recovered (mg/kg) Recovery %

Methamidophos 0.32 0.20 63

Limit of Quantitation (LOQ): Methamidophos = 0.05 mg/kg

Methodology: The laboratory 'in-house' method is available on request.

Sample retention: Retention samples will be discarded four weeks from date on report of analysis unless the client directs otherwise.

Signed (Analyst):

Neil J. Mora, NZCS Chemistry,
 Technical Officer.

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CONDITIONS OF ANALYSIS-GC

Date: 13 September 1999

Lab No.: GC99/4495

ANALYSIS: Methamidophos

Client: Crop & Food Research
PALMERSTON NORTH

Instrument: GC-17A

Sample matrix: Capsicum

Column: Length = 30m, Internal Diameter = 0.25 mm DB5-MS (0.25 µm)

Column temperature: Programmed from 130 to 160°C. Rate = 10°C/min.
Initial = 1.0min. Final = 6.0min.

Injection temperature: 180°C

Gas flows: Column flow = 1.04 mL/min. Helium

Detection systems: Flame Thermionic Temperature 250°C
Hydrogen = 3.5 mL/min. Air = 110 mL/min.
Range = 1 x 10 Current = 50

Sample size: 1.35 mg sample injected (0.5 µL)

Injection method: Syringe AOC-20i. Split. Ratio = 1:2

Accessories used: Class-GC10

Method: Metham1.MET

Signed (Analyst): 
Neil J. Mora

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