

THIAMETHOXAM (245) and CLOTHIANIDIN (238)

First draft prepared by Ms T. van der Velde-Koerts, Centre for Substances and Integrated Risk Assessment, National Institute of Public Health and the Environment, The Netherlands

EXPLANATION

Thiamethoxam and clothianidin were evaluated for toxicology and residues as a new compound in 2010, with many MRL recommendations. Additional residue data for both compounds were evaluated in 2011. The residue definition for thiamethoxam in plant commodities for enforcement is thiamethoxam, while the residue definition for dietary risk assessment is thiamethoxam and the metabolite CGA322704 (clothianidin), considered separately. The residue definition for clothianidin in plant commodities for enforcement and dietary risk assessment is clothianidin.

At the 2010 JMPR Meeting, a Codex MRL of 0.01* mg/kg for thiamethoxam and 0.01* mg/kg for clothianidin were recommended based on thiamethoxam use on papaya. Subsequent to the 2010 JMPR meeting a more critical GAP for the use of thiamethoxam on papaya was supported by the Brazilian authorities. Residue trials were conducted in 2006 to support the use on papaya and summaries of the trials have been provided to support a revised Codex MRL for thiamethoxam and clothianidin on papaya.

RESIDUE ANALYSIS*Analytical methods*

The Meeting received descriptions of the thiamethoxam analytical methods used for analysis of papaya samples from the trials.

HPLC-MS-MS method POPIT MET.078

HPLC-MS-MS method POPIT MET.078 Rev.03 [Marconi, 2006] was developed to analyse thiamethoxam and its metabolite CGA 322704 in plant materials. Samples were extracted with methanol:water (1:1 v/v) and an aliquot was evaporated and re-dissolved in water:acetonitrile (4:1 v/v). The resulting solution was filtered and analytes were quantified by HPLC-MS-MS using m/z 292 to 211 for thiamethoxam and m/z 250 to 132 for CGA 322704. The reported LOQ was 0.01 mg/kg in papaya. The validation results are presented in Table 1.

Table 1 Validation results for HPLC-MS-MS method POPIT MET.078 Rev 03

Commodity	Analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD _r	control samples mg/kg (n)	Calibration
					mean	range			
papaya whole fruit	thiamethoxam	0.01	0.011	7	85	79-90	5%	< 0.3LOQ	6 triplicate standards in solvent; 0.25 – 7.0 ng/mL; linear, R ² > 0.99
			0.11	5	81	79-86	3%		
			1.1	7	91	84-95	4%		
papaya pulp	CGA 322704	0.01	0.011	7	77	72-85	7%	< 0.3LOQ	idem
			0.11	5	78	76-80	2%		
			1.1	7	103	95-107	4%		
papaya pulp	thiamethoxam	0.01	0.011	7	86	80-99	7%	< 0.3LOQ	idem
			0.111	5	83	80-87	4%		
			0.11	5	80	77-83	3%		

USE PATTERN

A new more critical GAP has become available for registered use of thiamethoxam on papaya in Brazil (Table 2). An original label for this use was available and was confirmed by the Brazilian authorities.

Table 2 Registered pre-harvest uses of thiamethoxam

Crop	Country	Form (g ai/kg)	Application				PHI, days
			Method	Rate kg ai/ha	Spray conc, kg ai/hL	Number (interval)	
Papaya	Brazil	250 WG	1 soil drench + 2 foliar sprays	1× 0.1-0.2 + 2× 0.050	NS + 2x 0.0050-0.0083	1 + 2 (interval 16 days) ^a	14

NS = not specified.

^a. The minimum interval between the soil drench application and the first foliar application is not specified.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised residue trials on papaya conducted in Brazil in 2006. Results are presented in Table 3.

Table 3 Residues of thiamethoxam after pre-harvest treatment of papaya (whole fruit)

Location, year, (variety)	Form	No	Inter val (days)	kg ai/ha	kg ai/hL	method, last application	DAT	parent, mg/kg	CGA322704 mg/kg	Trial
Aracruz, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-	0.20	-	(a) 9 Oct; BBCH 81-85	0	0.14	0.010	LZF1
		F1-	31-14-	0.050			1	0.12	0.015	
		D2-	14	0.20			3	0.08	0.015	
		F2-		0.050			5	0.025	0.010	
		F3-		0.050			7	0.025	0.015	
Linhares, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-	0.20	-	(a) 9 Oct BBCH 81-85	0	0.24	0.010	LZF2
		F1-	31-14-	0.050			1	0.16	0.015	
		D2-	14	0.20			3	0.075	0.020	
		F2-		0.050			5	0.055	0.015	
		F3-		0.050			7	0.055	0.020	
Sooretame, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-	0.20	-	(a) 9 Oct BBCH 81-85	0	0.14	0.010	LZF3
		F1-	31-14-	0.050			1	0.11	0.010	
		D2-	14	0.20			3	0.075	0.010	
		F2-		0.050			5	0.065	0.010	
		F3-		0.050			7	0.065	0.020	
Jaguare, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-	0.20	-	(a) 9 Oct; BBCH 81-85	0	0.075	<0.01	LZF4
		F1-	31-14-	0.050			1	0.050	<0.01	
		D2-	14	0.20			3	0.040	<0.01	
		F2-		0.050			5	0.015	<0.01	
		F3-		0.050			7	0.010	0.010	
F4		0.050								

^a. Soil drenches (D) and foliar (F) applications in the sequence D1 – F1 – D2 – F2 – F3 – F4

^b. Results are the average of two replicate analytical samples.

[Marconi, 2006]. No unusual weather conditions. Plot size 100 m² (no of trees not indicated). Soil drench at 100 mL/plant and foliar spray volume 600 L/ha. Papaya samples (24 fruits from 12 plants, > 2 kg each) were harvested at maturity. Samples were stored deep-frozen at -20 °C for 8 months. Whole fruit samples and pulp samples were analysed in duplicate for parent and CGA 322704 using HPLC-MS-MS method POPIT MET.078 Rev 03. Results were not corrected for control levels (<0.01 mg/kg for each analyte) nor for average concurrent method recoveries (77%-103% for each analyte at 0.01, 0.1 and 1.0 mg/kg).

FATE OF RESIDUES IN STORAGE AND PROCESSING

Residues in the edible portion of food commodities

The Meeting received information on the distribution of residues in papaya pulp from supervised field trials conducted in Brazil in 2006. Results are presented in Table 4.

Table 4 Residues of thiamethoxam after pre-harvest treatment of papaya (pulp)

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	DAT	parent, mg/kg	CGA322704 mg/kg	Trial
Aracruz, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-31-14-14	0.20	0	0.025	<0.01	LZF1 (b)
		F1-		0.050	1	0.025	<0.01	
		D2-		0.20	3	0.025	<0.01	
		F2-		0.050	5	0.020	0.010	
		F3-F4		0.050	7	0.015	<0.01	
Linhares, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-31-14-14	0.20	0	0.025	<0.01	LZF2 (b)
		F1-		0.050	1	0.015	<0.01	
		D2-		0.20	3	0.020	0.010	
		F2-		0.050	5	0.020	0.010	
		F3-F4		0.050	7	0.020	0.010	
Sooretame, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-31-14-14	0.20	0	0.025	<0.01	LZF3
		F1-		0.050	1	0.025	<0.01	
		D2-		0.20	3	0.020	<0.01	
		F2-		0.050	5	0.020	<0.01	
		F3-F4		0.050	7	0.020	<0.01	
Jaguare, ES, Brazil, 2006, (Golden)	WG	D1-	30-29-31-14-14	0.20	0	<0.01	<0.01	LZF4
		F1-		0.050	1	<0.01	<0.01	
		D2-		0.20	3	<0.01	<0.01	
		F2-		0.050	5	<0.01	<0.01	
		F3-F4		0.050	7	<0.01	<0.01	

legends, see table 3

APPRAISAL

Thiamethoxam and clothianidin were evaluated for toxicology and residues as a new compound in 2010, with many MRL recommendations. Additional residue data for both compounds were evaluated in 2011. The residue definition for thiamethoxam in plant commodities for enforcement is thiamethoxam, while the residue definition for dietary risk assessment is thiamethoxam and the metabolite CGA322704 (clothianidin), considered separately. The residue definition for clothianidin in plant commodities for enforcement and dietary risk assessment is clothianidin.

At the 2010 JMPR Meeting, a Codex MRL of 0.01* mg/kg for thiamethoxam and 0.01* mg/kg for clothianidin were recommended based on thiamethoxam use on papaya. Subsequent to the 2010 JMPR meeting a more critical GAP for the use of thiamethoxam on papaya was supported by the Brazilian authorities. Residue trials were conducted in 2006 to support the use on papaya and summaries of the trials have been provided to support a revised Codex MRL for thiamethoxam and clothianidin on papaya.

Methods of Analysis

The methods reported to the Meeting and used in the supervised residue trials, determined parent thiamethoxam and the metabolite CGA 322704 (clothianidin). Samples were extracted with methanol:water. The final residue could then be determined by HPLC-MS-MS. The Meeting considers validation sufficient for papaya with an LOQ of 0.01 mg/kg for parent and its metabolite, each.

Stability of pesticide residues in stored analytical samples

At the 2010 JMPR, thiamethoxam and clothianidin were shown to be stable for 1-2 years when stored frozen at -10 °C or lower for a large range of commodities.

Results of supervised trials on crops

The Meeting received supervised field trials data for thiamethoxam use on papaya in Brazil.

Critical GAP for papaya in Brazil is for 1 soil drench application at 0.2 kg ai/ha followed by 2 foliar spray applications (interval 16 days) at 0.050 kg ai/ha and PHI 14 days. Trials from Brazil (1 drench at 0.20 kg ai/ha, 1 foliar spray at 0.050 kg ai/ha, 1 drench at 0.20 kg ai/ha plus 3 foliar sprays at 0.050 kg ai/ha and PHI up to 7 days) did not match this GAP. Because both the number of applications and the PHI do not match cGAP, it is not possible to use the proportionality approach.

Trials in/on papaya submitted for the 2010 JMPR supported only drench applications and were used to set the current MRL of 0.01* mg/kg for thiamethoxam and clothianidin.

The Meeting agreed that the Brazilian datasets for papaya matching Brazilian GAP could not be used to support a higher papaya maximum residue level recommendation. The Meeting confirmed its previous maximum residue level recommendation of 0.01* mg/kg thiamethoxam on papaya and 0.01* mg/kg clothianidin on papaya.

REFERENCES

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
-	Marconi F	2006.	Actara 250 WG – Magnitude de Resíduos de Thiamethoxam e CGA322704 em mamão – Brasil 2006. Syngenta, Sao Paulo, Brazil, study number M05071, 29 June 2007. GLP, Unpublished.