EVALUATION OF PESTICIDE RESIDUES IN SPICES

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EXPLANATION

The 2004 JMPR estimated maximum residue levels of pesticides in or on spices on the basis of monitoring results, and recommended that the maximum residue levels should be estimated to cover 95% of the residue population at 95% confidence level. The CCPR at its Thirty-sixth Session proposed that commodity group A028 be subdivided into sub-groups based on the parts of plants from which they are obtained – seeds, fruits or berries, roots or rhizomes, bark, buds, arils and flower stigmas – and that MRLs for pesticides that had been evaluated within the Codex system should be set for these sub-groups rather than for each of the pesticide–spice combinations[15].

The present Meeting followed the same principles which were applied by the 2004 JMPR and endorsed by the CCPR.

Registered use of some pesticides on peppers and monitoring data on spices were submitted by Thailand[16].

The European Spice Association presented the results of a survey on the effect of dehydration on some fresh spices. This information was evaluated by the present Meeting.

METHODS OF RESIDUE ANALYSIS

The on-line multi residue methods applied for the determination of pesticide residues is based on extraction with a mixture of acetone, dichloromethane and sodium chloride water solution. The concentrated extract is cleaned up on silica gel column and detection with GC-ECD (Steinwandter, 1985).

The carbendazim residues were extracted with acetone + sulphuric acid and partitioned with dichloromethane (Wong), or determined with the QUECHER method (Anastassiades *et al.*, 2003). Captan residues were also determined with the QUECHER method.

The recoveries of pesticides and the LOQ values reported are summarised in Table 1. No information was provided on the detection conditions or confirmation of the detected residues.

Table 1 Recovery and LOQ values reported for various pesticide spice commodity combination

Compound	Commodity	Spike level mg/kg	Recovery range%	LOQ mg/kg
Pyrethroids	ginger root, galangal rhizome, pepper black and white	0.01–0.05	73–115	0.01–0.05 0.03
	pepper black and white	0.1–0.5 1.0	72–76.7–91.4108	
	galangal rhizome, turmeric root	0.2	93.4–100.4	0.05
	kra-chai	0.2	78–92	0.02
Organophosphates	ginger root,	0.02 0.05 0.2 1	109–119 84.7–108.1 85.8–99.9 80–82.4	0.02–0.05
	galangal rhizome	0.05 0.2 1	90–105.1 87–101.1 82.7–96.5	0.05
	pepper black and white	0.05–0.1	85–117	0.07

[15] ALINORM 04/24, para 236

[16] Thailand: Summary of spices monitoring data, unpublished 2010

Compound	Commodity	Spike level mg/kg	Recovery range%	LOQ mg/kg
	Turmeric root	0.2	77–109	0.02
	kra-chai	0.2	81–95	0.02
	pepper black and white	0.05 0.2 1	81–96.5 82.4–93.4 80–90.3	0.02
Carbamates	ginger root, galangal rhizome, pepper black and white	0.05 0.2	85–118 76–92	0.02
	ginger root	0.05 0.1	82.5–93.1 72–79	0.1
	galangal rhizome	0.05 0.1	80.2–90.8 71–82	0.1
	turmeric root	0.2	64–87	0.1
	kra-chai	0.2	75–82	0.1
	pepper black and white	0.05 0.1	95.6–103.8 689–88	0.05
Carbendazim	ginger root, galangal rhizome pepper black and white	0.02	75	0.01
	ginger root	0.6	50–65	0.1
	galangal rhizome	0.2–5.0	64–105	0.2
	turmeric root	0.2–5.0	66–101	0.2
	kra-chai	0.2–5.0	67–105	0.2
	pepper black and white	0.1–1.0	58–71	0.1

USE OF PESTICIDES ON SPICES

In Thailand spices are mainly produced by small-scale farmers. Ginger and pepper are produced commercially mainly in the northern and eastern/southern regions of Thailand, respectively. Some ginger and pepper are also grown together with other fruits and vegetables, spices and herbs. Galangal, turmeric and Kra-Chai are mainly grown together with other fruits and vegetables, spices and herbs in all regions.

There are few registered uses of pesticides on spices in Thailand. Only pepper appeared on current pesticide label/recommendations which are given in Table 2.

Pesticide (common name)	Formulation	Dilution / Dose	(PHI)
benomyl	50 % WP	10 g ai/ 20 L water	
cadusafos	10 % GR	3–4 g ai/ 1 m^2 area around the plant	
carbofuran	3 % GR	0.45 g ai/ plant when planting	
ethoprofos	10 % GR	2–4 g ai/ 1 m^2 area around the plant	30
fenamiphos	10 % GR	3–4 g ai/ 1 m^2 area around the plant	60–90
metalaxyl	5 % GR	0.2 g ai/ plant	
phosphorous acid	40 % W/V SL	20 g ai/ 20 L water	
prochloraz	50 % WP	10 g ai/ 20 L water	14

The use of cadusafos, ethoprofos and fenamiphos 10% GR are for soil application to control nematodes. The treatment involves evenly applying the granules to the soil surface around the base of the tree, incorporating into the soil by mixing, followed immediately by irrigation. The 3–4 g ai dose is the dose per 1 square metre of the area at the tree base. The area of a tree base was approximately 0.5–1 square metre. The average number of pepper trees per 1 ha was 2500 trees. As the application dose per tree as 2–4 g ai the resultant treatment rates was approximately 5–10 kg ai/ha. The number of treatment per year was two (every 6 months).

Pesticides used by farmers on spices can be assumed to be comparable to other similar crops grown in the same area or on other crops grown with spices on the same farm.

Pesticides included in this monitoring programme were the major pesticides commonly used and were also occasionally found in many important fruits, vegetables, herbs and spice commodities in Thailand.

RESULTS OF MONITORING PESTICIDE RESIDUES IN SPICES

Pesticide residue data in on spices were reported from the 2005–2008 monitoring programmes. The analysis of samples during the periods of 2005–2006 and 2007–2008 were carried out by two laboratories applying basically similar methods. The LOQ values were generally substantially higher in the latter case. The summary of samples taken are shown in Table 2.

The monitoring programme included 38 pesticides which were commonly used in large amounts and their residues were occasionally found in many important fruits, vegetables, herbs and spice commodities in Thailand. The summary of the results of the analyses, which were not corrected for recoveries, is given in Table 3.

Table 2 Summary of number of spice samples analysed during 2005–2008 in Thailand

Commodity	Numbers of samples analysed		Total
	2005–2006	2007–2008	
Root or Rhizome spices			
Ginger , root	20	99	119
Galangal, rhizome	30	43	119
–Turmeric , root		45	45
Kra-Chai , root		44	44
Fruits and Berries Spices			
Pepper , Black	20	44	64
Pepper , White	20	42	62

Table 3 Summary of residue values detected in the monitoring programmes [a] in Thailand

	Ginger	Galangal rhizomes	Turmeric root	Kra-chai root	Pepper black	Pepper white
CNN	HS0784	HS0783	HS0794		HS0790	HS0790
No. Of samples analysed	119	73	45	44	64	62
Aldicarb [b]	0.02	0.02	-	-	0.07	0.07
Bifenthrin	0.05	0.05	0.05	0.05	0.03	0.03
Captan	0.05	0.05	-	**0.29**	-	-
Carbaryl	0.1	0.1	0.1	0.1	**0.14, 0.17, 0.35**	**0.09, 0.52, 0.78**
Carbendazim [b, c]	**0.01**	0.1	-	0.1	0.1	**0.01, 0.01, 0.01, 0.02**
Carbosulfan	0.1	0.1	0.1	0.1	0.07	0.07
Chlorpyrifos [c]	0.05	0.05	0.05	0.02	**0.02, 0.08, 0.02**	**0.04, 0.55,**
Cyfluthrin [b]	0.05	0.05	0.05	0.02	0.03	0.03
Cyhalothrin [b]	0.05	0.05	0.05	0.02	0.03	0.03
Cypermethrin [b]	0.05	0.05	0.05	0.02	**0.04, 0.05 (3), 0.07, 0.17, 0.13, 0.43**	**0.03**
Dichlorvos	0.05	0.05	0.05	0.02	0.02	0.02
Deltamethrin [b]	0.05	**0.18, 0.33**	0.05	0.02	0.03	0.03
Diazinon	0.05	0.05	0.05	0.02	0.07	0.07
Dicrotophos	0.05	0.05	0.05	0.02	0.07	0.07
Dimethoate	0.05	0.05	0.05	0.02	0.07	0.07
Ethion[2]	0.05	0.05	0.05	0.02	**0.05**	0.02
Fenitrothion	0.05	0.05	0.05	0.02	0.07	0.07
Fenobucarb	0.02	-	-	0.02	0.07	0.07
Fenvalerate	0.05	0.05	0.05	0.02	0.02	0.03
Isoprocarb	0.1	0.1	0.1	0.1	0.07	0.07
Malathion	0.05	0.05	0.05	0.02	0.07	0.07

	Ginger	Galangal rhizomes	Turmeric root	Kra-chai root	Pepper black	Pepper white
CNN	HS0784	HS0783	HS0794		HS0790	HS0790
Methidathion	0.05	0.05	0.05	0.02	0.02	0.02
Methiocarb [b]	0.1	0.1	0.1	0.1	0.07	0.07
Methomyl [b]	0.1	0.1	**0.69, 0.94, 1.47**	0.1	0.07	0.07
Omethoate	0.05	0.05	0.05	0.02	0.02	0.02
Oxamyl [b]	0.05	0.05	-		0.07	0.01
Permethrin [b]	0.05	0.05	0.05	0.02	0.03	0.07
Phosalone	0.05	0.05	0.02	0.02	0.02	0.02
Pirimiphos-ethyl	0.05	0.05	0.02	0.02	0.07	0.07
Pirimiphos-methyl	0.05	0.05	0.02	0.02	0.07	0.07
Profenofos	0.05	0.05	0.02	0.02	0.07	0.07
Promecarb	0.1	0.1	0.1	0.1	0.05	0.1
Prothiofos	0.1	0.1	0.02	0.02	0.07	0.07
Triazophos	0.1	0.1	0.02	0.02	0.07	0.07

[a] The residues measured are indicated with bold face, the LOQ values reported are shown with normal fonts.

[b] The definition of residue:

Aldicarb: Sum of aldicarb, aldicarb sulphoxide and aldicarb sulphone, expressed as aldicarb

Carbendazim: Sum of benomyl, carbendazim and thiophanate-methyl, expressed as carbendazim

Cyfluthrin: sum of isomers

Cyhalothrin: sum of isomers

Deltamethrin: Sum of deltamethrin, alpha-R- and trans-deltamethrin (1R-[1alpha(R*),3 alpha]]-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid, cyano(3-phenoxyphenyl)methyl ester and [1R-[1alpha(S*),3beta]]-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid, cyano(3-phenoxyphenyl) methyl ester)(fat-soluble)

Methiocarb: Sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb

Methomyl: Sum of methomyl and thiodicarb, expressed as methomyl

Oxamyl: Sum of oxamyl and oxamyl oxime, expressed as oxamyl

Permethrin: sum of isomers

[c] The reported LOQ values mg/kg for peppers black and white were:

carbaryl, chlorpyrifos: 0.07;

carbendazim: 0.01, cypermethrin: 0.03; ethion: 0.02

FATE OF RESIDUES IN STORAGE AND PROCESSING

The European Spice Association presented the results of a survey on the effect of dehydration on some fresh spices. Taking into consideration that different drying processes may result in different dehydration factors, the average of reported values were calculated. The rounded results (Weber, 2008) are presented in Table 4 below.

Table 4 Dehydration factors for some spices

Product name	Dehydration factor
Basil	7
Celery leaves	10
Chervil	5
Coriander leaves	13
Dill tops	7
Garlic	3
Laurel leaves	7
Marjoram	7
Onion	9
Oregano	6
Parsley leaves	6
Mint	7
Capsicums	10

Product name	Dehydration factor
Rosemary	7
Sage	7
Savoury herb	7
Tarragon	7
Thyme	7

APPRAISAL

Thailand submitted residue data obtained from 407 spice samples collected within a targeted monitoring programme carried out during 2005–2008.

Methods of analysis

The samples were analysed in two accredited laboratories applying either multi-residue methods based on acetone/dichloromethane/sodium chloride water solution extraction and partition and GC-ECD, GC FPD or HPLC detection after post-column derivatisation, or using the QUECHER method with HPLC-UV or HPLC-MSD detection. The recoveries reported were comparable, but the LOQ values were substantially higher in 2007–2008 than the earlier years.

No information was provided on the storage conditions and duration between sampling and analyses.

The residues and metabolites analysed are in accord with the residue definitions recommended by the JMPR.

Results of monitoring programmes

The monitoring programme included root or rhizome spices (ginger, turmeric root, kra-chai root and galangal rhizomes), fruit or berry spices (pepper - black and white) and 38 pesticides which were commonly used and where residues were occasionally found in fruits, vegetables, herbs and spice commodities in Thailand. The LOQ values obtained during method validation were often higher than the residue concentrations determined in the samples.

None of the samples contained detectable residues of the following pesticides which had been evaluated by the JMPR: aldicarb, bifenthrin, carbendazim, carbosulfan, cyfluthrin, cyhalothrin, dichlorvos, diazinon, dimethoate, fenitrothion, fenvalerate, malathion, methidathion, methiocarb, omethoate, oxamyl, permethrin, phosalone, pirimiphos-methyl, profenofos and triazophos.

Dicrotophos, fenobucarb, isoprocarb, pirimiphos-ethyl, promecarb and prothiofos residues were also looked for but the samples analysed did not contain detectable residues. As these compounds have not been evaluated by the JMPR, maximum residue levels could not be estimated.

Detectable residues were found in the following commodity pesticide combinations:

- Kra-chai root – captan: < 0.05 (43) and 0.29 mg/kg;
- Galangal root – deltamethrin: < 0.05 (71), 0.18, 0.33 mg/kg
- Turmeric root – methomyl: < 0.1 (42), 0.69, 0.94 and 1.47 mg/kg
- Pepper, black and white – carbaryl: 0.09, < 0.1 (120), 0.14, 0.17, 0.35, 0.52, and 0.78 mg/kg
- Pepper, black and white – carbendazim: < 0.1 (122), 0.01, 0.01, 0.01 and 0.02 mg/kg
- Pepper, black and white – chlorpyrifos: 0.02, 0.02, 0.04, < 0.07 (121), 0.08, and 0.55 mg/kg

- Pepper, black and white – cypermethrin: 0.03, < 0.03 (117), 0.04, 0.05 (3), 0.07, 0.17, 0.13, and 0.43 mg/kg
- Pepper, black – ethion: < 0.02 (63) and 0.05 mg/kg

The Meeting noted that the number of samples analysed for captan in kra-chai and for methomyl in turmeric root did not meet the minimum sample size requirement of 58 (JMPR Manual 2nd ed. Section 6.11.1 page 107), therefore no recommendation could be made for these combinations.

Taking into account the number of residue data enabled the estimation of maximum residue levels covering the 95–< 98% of the potentially present residues only, the Meeting included also the highest residue value in the estimated maximum residue level.

For fruit or berry and root and rhizome subgroups there are CXLs indicated in brackets, respectively, for chlorpyrifos (1; 1 mg/kg), cypermethrin (0.1; 0.2 mg/kg), dichlorvos (0.1; 0.1 mg/kg), diazinon (0.1; 0.5 mg/kg), dimethoate (0.5; 0.1 mg/kg), ethion (5; 0.3 mg/kg), fenitrothion (1; 0.1 mg/kg), malathion (1; 0.5 mg/kg), permethrin (0.05*; 0.05* mg/kg), phosalone (2; 3 mg/kg) and pirimiphos-methyl (-; 0.5 mg/kg) which cover the residues found in the Thai monitoring programme. These CXLs were confirmed by the present Meeting

For cypermethrin the Meeting estimated, for the fruit and berry subgroup a maximum residue level, median residue and HR of 0.5 mg/kg, 0.05 mg/kg and 0.43 mg/kg, respectively, and withdrew its previous recommendation of 0.1 mg/kg for the maximum residue level.

On the basis of the monitoring data, the Meeting concluded that the residue concentrations listed below were suitable for establishing MRLs and for assessing IEDIs and IESTIs.

RECOMMENDATIONS

Maximum, HR and STMR residue values recommended for fruit or berry and root and rhizome spices.

Codex Number	Commodity	Pesticide	Maximum residue level (mg/kg)		Median residue mg/kg	HR mg/kg
			New	Previous		
028B	Fruit or berry	Carbaryl	0.8		0.1	0.78
		Carbendazim	0.1		0.1	0.1
		Cypermethrin	0.5	0.2	0.05	0.43
0.28D	Root and rhizome	Deltamethrin	0.5		0.05	0.33

Taking into account that sufficient number of random samples were analysed and no detectable residue was found in any of the samples, the Meeting estimated maximum residue, median and high levels in root and rhizome and fruit or berry spice groups at the reported highest LOQ values shown in the table below:

Maximum, median and high residue values [mg/kg] based on LOQ of pesticides

	028D Root and rhizome spices	028B Fruit and berry
Aldicarb	0.02	0.07
Bifenthrin	0.05	0.03
Captan	0.05	-
Carbaryl	0.1	
Carbendazim	0.1	
Carbosulfan	0.1	0.07

	028D Root and rhizome spices	028B Fruit and berry
Cyfluthrin	0.05	0.03
Cyhalothrin	0.05	0.03
Deltamethrin		0.03
Fenvalerate	0.05	0.03
Methidathion	0.05	0.02
Methiocarb	0.1	0.07
Methomyl		0.07
Omethoate	0.05	0.02
Oxamyl	0.05	0.07
Profenofos	0.05	0.07
Triazophos	0.1	0.07

DIETARY RISK ASSESSMENT

The Meeting concluded that, it is unlikely that the dietary intake estimated by previous meetings would be markedly affected by the consumption of food containing spices considered by the present meeting.

REFERENCES

Thailand: Summary of spices monitoring data, unpublished 2010

Steinwandter, H. 1985. Universal 5 min on line Method for Extracting and Isolating Pesticide Residues and Industrial Chemicals. Freserius Z. Anal. Chem. No. 1155

Sue-Sun Wong. Liquid Chromatographic Determination of Carbendazim in Fruits and Vegetables. Taiwan Agricultural Chemicals and Toxic Substances Research Institute, unpublished

Anastassiades, M., S. Lehotay, D. Stajnbaher and F. Schenck (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J AOAC Int 86(2): 412-431.

Weber G., 2008, Letter to the editor European Spice Association, ESA, recommends dehydration factors to assess pesticide residues on products of the spice industry, Deutsche Lebensmittel-Rundschau, 475-476.