

**DITHIOCARBAMATES (105)****MANCOZEB (050) and MANEB (-)**

*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**

Dithiocarbamate fungicides were evaluated several times by the JMPR for toxicology and residues. In 1993, the JMPR derived an ADI of 0–0.03 mg/kg bw for dithiocarbamate pesticides as mancozeb and maneb based on thyroid toxicity. For their metabolite ethylenethiourea (ETU), an ADI of 0–0.004 mg/kg bw has been allocated.

Dithiocarbamate pesticides were listed by the Forty-third Session of the CCPR for evaluation of additional commodities by the 2012 JMPR. The Meeting received information on residue analysis and supervised trials with mancozeb and maneb on okra.

**RESIDUE ANALYSIS*****Analytical methods***

The analytical method used for the supervised trials on okra is based on the conversion of the residue of dithiocarbamate pesticides (as mancozeb and maneb) to CS<sub>2</sub> and detection with GC-MS. This method has been validated on a wide range of crops and substrates (JMPR 1993). Mancozeb and maneb were extracted from okra samples (a minimum of cutting was made) using a solution of tin(II)chloride in HCl and trimethylpentane (TMP). After incubation at 80 °C for 1 hour (shaking every 20 minutes), samples are cooled and analysed for CS<sub>2</sub> using GC-MS.

Recoveries were carried out with thiram instead of mancozeb or maneb. Samples were fortified using a thiram solution in acetone (0.5 mg/kg). The LOQ for the analysis of total dithiocarbamates was reported as 0.05 mg/kg, but the lowest fortification level was 0.5 mg/kg (Henderson, 2003 and 2005).

Residue supervised trials samples were analysed for dithiocarbamates using GC-MSD (Direct Laboratories, 2006). It is not clear whether results are corrected for control levels or for individual concurrent method recoveries. The method validation for the analysis of the okra field samples showed mean recoveries of 80 % (76–82%, n = 19) or 95% (94–104 %, n = 21) after fortification with 0.5 mg/kg.

Field samples were stored at -20 °C for 86–93 days in the first trial period and 48–81 days in the second trial period. No information on storage stability was reported.

**USE PATTERN**

The intended use pattern for okra in Côte d'Ivoire was provided as part of the field trials conducted within the Pesticide Initiative Programme of COLEACP<sup>1</sup> aiming to provide data for establishing import MRLs in the European Union. The application conditions were based on the requirement of appropriate control of diseases, but they were not supported by label or official declaration of the approved use.

---

<sup>1</sup> The COLEACP is a professional association with the objective to harmonise the relationships between producers and exporters from African, Caribbean and Pacific countries (ACP) and EU importers.

A proposal for critical GAP in Côte d'Ivoire described the use of mancozeb and maneb on okra as: application rate 2 kg ai/ha, PHI 7 days, 2 treatments with 14 days intervals between treatments (COLEACP 2011).

## RESIDUE RESULTING FROM SUPERVISED TRIALS ON CROPS

### Okra

The Meeting received supervised residue trials of ground treatments of mancozeb or maneb for okra. The results are summarized in Tables 1 and 2. Application rates were reported as mancozeb or maneb (parent). Unquantifiable residues are shown as below LOQ (< 0.05 mg/kg, expressed as CS<sub>2</sub>).

Okra shoots are not all harvested on the same day but every few days. First harvest starts approximately 45 days after sowing; full harvest is at approximately 60 days after sowing.

Residue trials on okra were conducted in two sites in Côte d'Ivoire, in two sowing seasons of 2004 (dry season in April/May and rainy season in August/September) [Delhove, 2005]. Mancozeb or maneb in combination with several other pesticides (six combinations) was used particularly shortly before and during the harvest phase (Delhove, 2005).

Table 1 Residues of mancozeb in okra, whole fruit

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	Information on growth stage at last treatment	PHI (days)	Residues (mg/kg)	Reference
Combination 1: beta-cyfluthrin, bifenthrin, carbofuran, difenoconazol, dimethoate, imidacloprid, <b>mancozeb</b> , mefenoxam, sulphur, thiamethoxam, thiophanate									
Côte d'Ivoire, Dabou, 2004 (Indiana)	WP	2	14	2.1 2.1	0.4 0.3	Growing fruits	2 7	1.87 <sup>a</sup> 0.13 <sup>a</sup>	Delhove, 2005
Côte d'Ivoire, Abengourou, 2004 (Indiana)	WP	2	14	2.1 2.1	0.4 0.3	Growing fruits	3 7	0.41 <sup>b</sup> 0.05 <sup>b</sup>	Delhove, 2005
Combination 2: abamectin, beta-cyfluthrin, bifenthrin, cadusafos, carbendazim, chlorpyrifos-ethyl, chlorothalonil, diazinon, imidacloprid, malathion, <b>mancozeb</b> , sulphur, thiophanate									
Côte d'Ivoire, Dabou, 2004 (Indiana)	WP	2	14	2.0 2.1	0.2 0.5	Growing fruits	8 14	0.11 <sup>a</sup> <LOQ <sup>a</sup>	Delhove, 2005
Ivory Coast, Abengourou, 2004 (Indiana)	WP	2	14	2.3 2.1	0.6 0.4	Growing fruits	7 14	0.06 <sup>a</sup> 0.13 <sup>a</sup>	Delhove, 2005
Combination 4: azoxystrobin, beta-cyfluthrin, bifenthrin, carbendazim, carbofuran, chlorothalonil, deltamethrin, difenoconazol, dimethoate, imidacloprid, thiophanate-methyl, <b>mancozeb</b> , mefenoxam, thiamethoxam									
Côte d'Ivoire, Dabou, 2004 (Indiana)	WP	1	-	2.0	0.4	Mature fruits	2 7	0.37 <sup>a</sup> <LOQ <sup>a</sup>	Delhove, 2005
Côte d'Ivoire, Abengourou, 2004 (Indiana)	WP	1	-	2.1	0.4	Mature fruits	2 7	1.97 <sup>b</sup> <LOQ <sup>b</sup>	Delhove, 2005
Combination 5: beta-cyfluthrin, bifenthrin, cadusafos, carbendazim, chlorothalonil, cypermethrin, deltamethrin, imidacloprid, malathion, <b>mancozeb</b> , thiophanate-methyl									
Côte d'Ivoire, Dabou, 2004 (Indiana)	WP	3	14 7	1.8 2.1 2.0	0.5 0.5 0.5	Mature fruits	7 14 21	0.13 <sup>a</sup> <LOQ <sup>a</sup> <LOQ <sup>a</sup>	Delhove, 2005
Côte d'Ivoire, Abengourou, 2004 (Indiana)	WP	3	14 7	2.0 2.0 2.0	0.6 0.5 0.5	Mature fruits	7 14 21	NA <LOQ <sup>a</sup> <LOQ <sup>b</sup>	Delhove, 2005

<sup>a</sup> sample size 500 g <sup>b</sup> sample size 165 g

Table 2 Residues of maneb in okra, whole fruit

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	Information on growth stage at last treatment	PHI (days)	Residues (mg/kg)	Reference
Combination 3: abamectin, azoxystrobin, bifenthrin, carbosulfan, cypermethrin, lambda-cyhalothrin, malathion, maneb, copper oxychloride, sulphur, spinosad, thiamethoxam									
Côte d'Ivoire, Dabou, 2004 (Indiana)	WP	2	14	2.040 2.100	0.2 0.5	Mature fruits	8 14	<LOQ <sup>a</sup> <LOQ <sup>a</sup>	Delhove, 2005
Côte d'Ivoire, Abengourou, 2004 (Indiana)	WP	2	14	2.335 2.100	0.6 0.4	Mature fruits	7 14	<LOQ <sup>a</sup> <LOQ <sup>a</sup>	Delhove, 2005
Combination 6: azoxystrobin, bifenthrin, carbendazim, carbosulfan, chlorpyrifos, cypermethrin, L-cyhalothrin, malathion, maneb, copper oxychloride, sulphur, spinosad, thiamethoxam, thiophanate-methyl									
Côte d'Ivoire, Dabou, 2004 (Indiana)	WP	4	10 14 7	2.027 1.790 2.054 2.050	0.6 0.5 0.5 0.5	Mature fruits	7 14	NA <LOQ <sup>a</sup>	Delhove, 2005
Côte d'Ivoire, Abengourou, 2004 (Indiana)	WP	4	10 14 7	2.003 2.012 2.024 2.046	0.6 0.6 0.5 0.5	Mature fruits	7 14	0.14 <sup>a</sup> <LOQ <sup>a</sup>	

<sup>a</sup> sample size 500 g

<sup>b</sup> sample size 165 g

Fruit samples of 6 kg (1 kg from each combination in each site) for the wet season and 2–6 kg for the dry season were taken. In the laboratory, samples were divided in two subsamples. Only one sample was analysed. According to the FAO Manual, samples with a minimum weight of 2 kg should be taken for the analysis of residues. The sample size taken in the residue trials is therefore too small. However, since okra fruits are small, samples  $\geq 0.5$  kg could be considered acceptable.

## APPRAISAL

Ethylene-bis-dithiocarbamate fungicides were evaluated several times by the JMPR for toxicology and residues. In 1993, the JMPR estimated a group ADI of 0–0.03 mg/kg bw for mancozeb, maneb, metiram and zineb.

Dithiocarbamate pesticides were listed by the Forty-third Session of the CCPR for evaluation of additional commodities by the 2012 JMPR. The Meeting received information on residue analysis and supervised trials with mancozeb and maneb on okra.

### Methods of Analysis

The analytical method used in the supervised trials of mancozeb and maneb in okra relied on CS<sub>2</sub> evolution using GC-MSD with a reporting limit for of quantification of dithiocarbamates of 0.05 mg/kg.

### Results of supervised trials on crops

The Meeting received supervised trial data for mancozeb and maneb on okra in Côte d'Ivoire. As part of the field trials conducted within the Pesticide Initiative Programme aiming to provide data for establishing import MRLs in the European Union, maneb and mancozeb were applied in combination with other pesticides as foliar spray treatment with up to three times at about 2 kg ai/ha in six trials carried out in Côte d'Ivoire. The residues were 7 days after one to three applications of mancozeb, < 0.05, 0.06, 0.11, 0.13 and 0.13 mg/kg and after two to four applications of maneb, < 0.05, < 0.05 and 0.14 mg/kg.

The application conditions were based on the requirement of appropriate control of diseases of okra, but they were not supported by a label or an official declaration of approved use from Côte d'Ivoire.

Because no official information on GAP was submitted, the Meeting could not estimate a maximum residue level for dithiocarbamates in okra.

## REFERENCES

Author	Year	Title
COLEACP	2011	Mancozeb, Maneb, Request for a Codex MRL. On behalf of COLEACP-PIP. Non-GLP. Unpublished
Delhove G	2005	Report on residue trials in Côte d'Ivoire on okra. PIP Pesticides residues trials programme. CI/AIPR/2004/03 Non GLP. Unpublished
Direct Laboratories	2006	Final Analytical Report for the analysis of pesticide residues in samples of Okra. COLE/ACP Ref: PIP No. 0106/22/Direct-Lab/03) and PIP No. 0106/22/Direct-Lab/05. GLP. Unpublished
Henderson K	2005	Standard Operating Procedure: Preparation of fruit and vegetables for pesticide residue analysis, edition 6. PRES/002. Non GLP. Unpublished
Henderson K	2003	Standard Operating Procedure: Extraction and determination of dithiocarbamate pesticide residues in fruit and vegetables, edition 6. PRES/007. Non-GLP. Unpublished