# PESTICIDES RESIDUE ANALYSIS OF FRUITS FOR FARM ACCREDITATION SCHEMES IN SABAH, MALAYSIA

**Alinah Abdul Rahman**

Agriculture Research Centre Tuaran, Sabah Department of Agriculture, P. O. Box 3, 80207 Tuaran, Sabah, Malaysia

Email: Alinah.Rahman@sabah.gov.my

## ABSTRACT

The Department of Agriculture Sabah initiated pesticide residue analysis in fruits for myGAP and myOrganic farm accreditation schemes since 2004 and 2010. Pesticides residue analysis is one of the requirements in the farm certification process. The aim of this project is to ensure the safety and quality of local agricultural produce. The approach is not only beneficial to consumers but also to the environment while ensuring no health implications on farmers and workers. From 2014 to 2018, a total of 176 samples of fruits out of 1,053 samples of agricultural produce have been analyzed for pesticides residue. Fruit samples were analyzed for ethylene bis-dithiocarbamates (EBDC), organophosphorus (OP), organochlorine (OC), and synthetic pyrethroid (SP) pesticides; commonly used by farmers in Sabah. The headspace method was used to analyze EBDC pesticides and the "quick, easy, cheap, effective, rugged, and safe" (QuEChERS) method for OP, OC, and SP pesticides. Of the 176 fruit samples analysed, 161 samples were for myGAP and 15 samples for myOrganic certifications. The violation rates over the five-year period for myGAP are 2% and for myOrganic, 7%. Of the 176 samples analyzed, 2% of the samples were found exceeding the maximum residue limit based on the 16th Schedule, Food Act 1983. Cypermethrin, chlorfenapyr, and dimethoate pesticides were detected in the 2% violated samples. To date, a total of 58 fruit orchards have been certified for farm accreditation schemes which covers an area of approximately 650 hectares. Seventy-one farms with an area of 243 hectares are at the auditing stage while 50 farms covering an area of 118 hectares are at the land inspection stage. The Department of Agriculture Sabah will continue to promote farm certification to educate farmers on the importance of Good Agricultural Practices (GAP) to enhance market acceptability of local agricultural produce to neighboring countries.

Keywords: pesticide residue, myGAP, myOrganic, maximum residue limit, cypermethrin, chlorfenapyr, dimethoate

## 1. INTRODUCTION

In Sabah, Malaysia and other tropical countries, pesticides are used extensively in agriculture for improving the quality of agricultural products and also increasing the yields. Pesticides play an important role in modern agriculture and are irreplaceable. However, most pesticides are toxic, environmentally stable, and are mobile substances in the environment, contaminating not only food crops but also soil, water, and air. Thus, good agricultural practices (GAP) were introduced with the aim to reduce excessive usage of pesticides in agriculture to ensure the safety and quality of agricultural produce.

In Malaysia, certification schemes such as GAP were introduced as one of the strategies not only to increase quality, safety, and environment-friendly products but also to satisfy consumer preferences and to enhance market acceptability of importing countries. The scheme is based

on the Malaysian Standard MS 1784:2005 *Crop Commodities – Good Agriculture Practices (GAP)* (Ministry of Agriculture Malaysia, 2014). The Malaysian Good Agricultural Practice (myGAP) is a voluntary scheme and is free of charge, where interested farms can register and undergo a series of steps before the farm can be accredited; e.g., site inspection by a soil team, pre-audit and sampling by internal auditors, follow-up audit by external auditors, recommendations for certification by a technical committee, and finally the awarding of myGAP or myOrganic certificate (Ministry of Agriculture Malaysia, 2014). The government provides free courses and trainings to the farmers. On the other hand, Malaysian Organic (myOrganic) is a rebranding of the organic certification scheme introduced by the Ministry of Agriculture to recognize farms that practice organic farming based on Malaysian Standard MS 1529:2015 *Plant-based organically produced foods-requirements for production, processing, handling, labelling and marketing (Ministry of Agriculture Malaysia)*. The implementation of myGAP and myOrganic schemes in agriculture has resulted in increased quality and safety of agricultural products and has provided consumers with better choices of products. Farm certification provides advantages not only to the consumers, but also to the farmers, workers, and the environment.

The Department of Agriculture Sabah has initiated the pesticide residue analysis in agricultural produce for the farm certification of myGAP and myOrganic since 2004 and 2010. Farmers are required to apply for farm certification through their respective district agricultural office before the food crops samples can be collected for analysis. All relevant documents are evaluated and the farms are inspected. Eligible farmers are given assistance and guidance while the farms are inspected by the soil survey and conservation teams. Pre-audit by the internal auditor at the district level are conducted once the initial inspections are accepted and passed. Food crops samples are harvested for pesticide residues and heavy metal analysis at the chemistry laboratory. After the pre-audit stage, external audit is carried out to ensure that the farmers are practising and complying with GAP in accordance to the specified standards. The final stage is the recommendation for farm certification by the technical committee at the national level (Ministry of Agriculture Malaysia, 2014). The aim of this project is to analyze pesticide residue in fruit samples for farm accreditation to ensure the safety and quality in local agricultural produce. In this paper, the analysis of pesticide residue in fruit samples received from 2014 to 2018 are discussed.

## 2. MATERIALS AND METHODS

### 2.1. Reagents and Chemicals

Pesticides standard (purity 98% and above) for organophosphorus (OP), organochlorine (OC), and synthetic pyrethroids (SP) were obtained from Dr. Ehrenstorfer, Augsburg, Germany. Analytical grade of anhydrous magnesium sulfate, anhydrous sodium acetate; and gas chromatography grade of acetone, acetonitrile, and hexane for OP, OC and SP analysis were obtained from Merck, Darmstadt Germany. Dispersive solid phase extraction kits were obtained from Agilent Technologies, USA. For the ethylene bis-dithiocarbamates analysis, 99% purity of carbon disulphide ($CS_2$), 5M hydrochloric acid and stannous (II) chloride were also obtained from Merck, Darmstadt Germany.

Pesticide stock solutions (500 ppm) were prepared by dissolving the appropriate amount of pesticide standards in acetonitrile for OP pesticides (18 active ingredients), hexane for OC (10 active ingredients), and SP (6 active ingredients) pesticides. Intermediate standard solutions with certain concentrations were prepared for each group of pesticides.

## 2.2. Sampling

Following the approval of myGAP and myOrganic certification schemes of the farmers whom applied through the district agricultural office, fruit samplings would take place. Samplings were carried out by the agricultural district staff after the pre-auditing stage and the samples were sent to the pesticide residue and foliar laboratory for analysis.

## 2.3. Analysis

The fruits samples were analyzed for EBDC, OP, OC, and SP pesticides which are commonly used by farmers in Sabah. The headspace method was used to analyze EBDC pesticides. EBDC in fruits is determined by the carbon disulfide formed during the heating of dithiocarbamates with stannous (II) chloride and hydrochloric acid in the head-space by gas chromatograph with flame photometric detector in the sulphur mode (McLeod & McCully, 1969). Fifty millilitre of distilled water and 50 mL of 2% $SnCl_2$/5M HCl mixture were placed in a 250 mL laboratory bottle containing 30 g fruit samples. The mixtures were thoroughly shaken by hand and placed in a water bath at 80 °C for one hour. The bottles were shaken every 30 minutes. The bottles were kept in an oven at 30 °C. The upper phase (gas form) was injected manually to Gas Chromatograph (GC-FPD) using gas tight syringe.

Analysis of OP, OC, and SP pesticides were carried out using the Official QuEChERS method by Lehotey *et al*. (2005). Fifteen grams of homogenized samples were weighed into 50 mL Teflon centrifuge tubes. Fifteen millilitres of acetonitrile containing 1% acetic acid were added into the samples and shaken vigorously for 30 seconds by hand followed by vortex mixing for 2 minutes. Extraction kit containing 6 g anhydrous magnesium sulphate and 1.5 g anhydrous sodium acetate were added and shaken vigorously for 30 seconds by hand followed by vortex mixing for 2 minutes. The extract was later centrifuged at 3000 rpm for 2 minutes. One milliliter of extract was transferred to d-SPE tubes and shaken vigorously for 30 seconds by hand followed by vortex mixing for 2 minutes. The extract was centrifuged again at 3000 rpm for 2 minutes. The supernatant at 200–300 µL was transferred into 2 mL vials with low-volume-inserts for the determination of pesticides using GC.

## 2.4. Apparatus and Instrumentation

A sample homogenizer (GM300, Retch Germany) was used to homogenize the fruit samples and a multi speed vortex mixer (Vortexer, Heathrow Scientific) was used for sample extraction. Centrifugation of the fruit extracts was performed using Kubota 4200 (for 50 mL tubes) and Gyrozen Micro Centrifuge (for 2 mL tubes). Waterbath (Memmert) and oven (Memmert) were used for EBDC sample preparation.

A gas chromatograph (Agilent Technologies 7890A & 7890B) equipped with Flame Photometric Detector (FPD) was used for the determination of OP pesticides. This instrument was equipped with a non-polar, fused-silica capillary column, HP5 (30 m × 0.32 mm × 0.25 µm) and polar fused-silica capillary column, DB1701 (15 m × 0.53 mm × 1.0 µm), obtained from Agilent Technologies USA. The HP5 column temperature was maintained at 110 °C for 0.5 min, and then programmed at 200 °C $min^{-1}$ to 170 °C for 0 min followed by another temperature ramp of 5 °C to 230 °C for 0 min and a final temperature ramp of 15 °C to 280 °C for 12 min. The DB-1701 column temperature was maintained at 130 °C for 0.5 min, and then programmed at 30 °C $min^{-1}$ to 190 °C for 3 min followed by another temperature ramp of 5 °C to 240 °C for 3 min and a final temperature ramp of 10 °C to 260 °C for 12 min. The injector and detector temperature were

maintained at 260 °C and 250 °C, respectively.

A gas chromatograph (Agilent Technologies 7890B) equipped with micro Electron Capture Detector was used for the determination of OC and SP pesticides. This instrument was equipped with a polar fused-silica capillary column, SPB-608 (30 m × 0.53 mm × 0.5 µm) obtained from J&W Scientific, USA and Ultra-1 (25 m × 0.32 mm × 0.52 µm) obtained from Agilent Technologies, USA. The SPB-608 column temperature was maintained at 150 °C for 0.5 min, and then programmed at 30° C $min^{-1}$ to 210°C for 2 min followed by another temperature ramp of 5 °C to 285 °C for 14 min. The Ultra-1 column temperature was maintained at 130 °C for 0.5 min, and then programmed at 30 °C $min^{-1}$ to 160 °C for 0 min followed by another temperature ramp of 5 °C to 280 °C for 5 min. The injector and detector temperature were maintained at 260 °C and 300 °C, respectively.

A gas chromatograph (Agilent Technologies 6890N) equipped with FPD with sulphur mode was used for the determination of EBDC pesticides in CS2 form. This instrument is equipped with a non-polar, fused-silica capillary column, HP5 (10 m × 0.53 mm × 2.65 µm). The HP5 column temperature is maintained at 60 °C for 0.5 min, and then programmed at 30 °C $min^{-1}$ to 230 °C. The injector and detector temperatures were maintained at 220 °C and 200 °C, respectively.

## 3. RESULTS AND DISCUSSION

A total of 1,053 samples of agricultural produce such as vegetables, fruits, and other food crops have been analyzed for myGAP and myOrganic farm certification schemes from 2014 to 2018. Of the 1,053 samples analyzed, 176 are fruits samples. A total of 18 districts in Sabah were involved in the pesticide residue analysis of fruit samples for farm certification schemes over the five-year period. The fruit samples were analyzed for EBDC, OP, OC, and SP pesticides, which were commonly used by farmers in Sabah. The headspace method was used to analyze EBDC pesticides and the official QuEChERS method (AOAC 2007.01) for OP, OC, and SP pesticides.

The summary of pesticides residue analysis results for myGAP and myOrganic samples categorized by types of fruits are shown in Table 1. The results of the analysis over the five-year period are summarized in Table 2. Of the 176 fruit samples analyzed, 161 (91%) samples were for myGAP and 15 (9%) samples for myOrganic certifications. The violation rates over the five-year period for myGAP were 2% and 7% for myOrganic. Overall, 2% (3 samples) of the 176 samples exceeded the MRL (Maximum Residue Limit) as stipulated in the 16th Schedule, Food Act 1983 (Ministry of Health, Malaysia). Dimethoate (OP pesticide), chlorfenapyr (OC pesticide) and cypermethrin (SP pesticide) were detected in the 2% violated samples. The violated samples were guava, 'Chok Anan' mango and salacca (*Salaca zalacca*). Guava and mango samples were from myGAP certification and salacca was from myOrganic certification. Dimethoate and chlorfenapyr were detected in guava samples meanwhile cypermethrin was detected in Chok Anan mango and salacca.

The total estimated hectarage of fruit farms in Sabah are approximately 18,100 ha with a producing area of 10,350 ha and a production of 108,150 tonnes (DOA/2018). To date, a total of 58 fruit farms have been certified for farm accreditation schemes which covers an area of approximately 650 hectares. Another 71 farms which covers an area of 243 hectares are still at the auditing stage while another 50 farms which covers an area of 118 hectares are at the land inspection stage. The 58 certified fruit farms only accounted for about 6% of the total producing area of fruits in Sabah.

The number of certified fruit farms in Sabah are still very low due to its voluntary basis for certification at the time being. The awareness on the importance and benefits of farm certification among the farmers and consumers are low. The Department of Agriculture Sabah needs to encourage food crop farmers to adopt GAP to ensure that their agricultural produce are of good quality and safe for consumption. Besides that, farm certification will improve the confidence of domestic and foreign markets on Sabah fruits and vegetables. This will also cater to the demand of importing countries for certified agricultural produce.

**Table 1: Pesticide residue analysis for myGAP and myOrganic categorized by types of fruits from 2014-2018**

| Types of Fruits | myGAP | | myOrganic | | Overall | |
|---|---|---|---|---|---|---|
| | No. of Samples Analyzed | No. of Samples > MRL | No. of Samples Analyzed | No. of Samples With Residue (Violation) | No. of Samples Analyzed | No. of Samples > MRL / Violation |
| Custard Apple | 1 | 0 | 0 | 0 | 1 | 0 |
| Avocado | 1 | 0 | 0 | 0 | 1 | 0 |
| Papaya | 9 | 0 | 0 | 0 | 9 | 0 |
| Durian | 6 | 0 | 3 | 0 | 9 | 0 |
| Soursop | 2 | 0 | 0 | 0 | 2 | 0 |
| Sweet Corn | 11 | 0 | 1 | 0 | 12 | 0 |
| Water Apple | 1 | 0 | 1 | 0 | 2 | 0 |
| Seedless Lemon | 0 | 0 | 2 | 0 | 2 | 0 |
| Guava | 24 | 2 (8%) Dimethoate (2) Chlorfenapyr (1) | 0 | 0 | 24 | 2 (8%) Dimethoate (2) Chlorfenapyr (1) |
| Sweet Orange cv. Madu | 2 | 0 | 0 | 0 | 2 | 0 |
| Mango cv. Chok Anan | 10 | 1 (8%) Cypermethrin | 0 | 0 | 10 | 1 (8%) Cypermethrin |
| Mango cv. Harumanis | 7 | 0 | 0 | 0 | 7 | 0 |
| Mangosteen | 2 | 0 | 2 | 0 | 4 | 0 |
| Passionfruit | 1 | 0 | 0 | 0 | 1 | 0 |
| Pineapple | 3 | 0 | 0 | 0 | 3 | 0 |
| Pamelo | 18 | 0 | 4 | 0 | 22 | 0 |
| Banana cv. Berangan | 7 | 0 | 0 | 0 | 7 | 0 |
| Plaintain Banana cv. Saba | 27 | 0 | 0 | 0 | 27 | 0 |
| Plaintain Banana cv. Sekaki | 1 | 0 | 0 | 0 | 1 | 0 |
| Pitaya | 8 | 0 | 1 | 0 | 9 | 0 |
| Rambutan | 4 | 0 | 0 | 0 | 4 | 0 |
| Rockmelon | 1 | 0 | 0 | 0 | 1 | 0 |
| Salacca | 3 | 0 | 1 | 1 (100%) Cypermethrin | 4 | 1 (25%) Cypermethrin |
| Watermelon | 10 | 0 | 0 | 0 | 10 | 0 |
| Jackfruit | 2 | 0 | 0 | 0 | 2 | 0 |
| Total | 161 | 3 (2%) | 15 | 1 (7%) | 176 | 4 (2%) |

**Table 2: Pesticide residue analysis for myGAP and myOrganic in fruit samples from 2014 to 2018**

| Types of Fruits | myGAP | | myOrganic | | Overall | |
|---|---|---|---|---|---|---|
| | No. of Samples Analyzed | No. of Samples > MRL | No. of Samples Analyzed | No. of Samples With Residue (Violation) | No. of Samples Analyzed | No. of Samples > MRL / Violation |
| 2014 | 14 | 0 | 7 | 1 (14%) | 21 | 1 (5%) |
| 2015 | 16 | 1 (6%) | 1 | 0 | 17 | 1 (6%) |
| 2016 | 29 | 0 | 5 | 0 | 34 | 0 |
| 2017 | 23 | 0 | 1 | 0 | 24 | 0 |
| 2018 | 79 | 2 (3%) | 1 | 0 | 80 | 2 (3%) |
| Total | 161 | 3 (2%) | 15 | 1 (7%) | 176 | 4 (2%) |

## 4. CONCLUSIONS

From 2014 to 2018, the overall violation rate for fruit farms certification in Sabah was at 2%. At present, the number of fruit farms in Sabah with myGAP and myOrganic certification are still very low with only 58 farms are certified. This achievement only accounted for about 6% of the total producing area of fruits in Sabah. The Department of Agriculture Sabah will continue to promote and to educate farmers on the importance of GAP in agriculture to ensure the quality and safety of our agricultural produce. Apart from that, more awareness campaigns on the advantages and benefits of farm certification will be organized. Technical support, training, and extension services to the farmers will also be provided.

## ACKNOWLEDGEMENT

The author wishes to thank the Director of Agriculture Sabah, Mr. Muhidin Hj. Ismail, and the Deputy Director of Agriculture (Research), Mr. Chong Tan Chun, for permission to publish this paper. Thanks is also due to the Assistant Director (Research), Mr. Teo Su Sin, for contributing ideas, editing, and proof-reading this manuscript. Special thanks and acknowledgement goes to all the pesticide residue laboratory staff for their commitment and hard work in the pesticide residue analysis. The author would also like to thank Agriculture Officer (Farm Accreditation), Mr. Mohd. Nazih Fikriandi Kaliwon, for providing the farm certification updates and Acting Agriculture Officer, Ms. Viviana Lasimin, for providing the statistical data.

## REFERENCES

Department of Agriculture Sabah. (2017). *Skim Amalan Pertanian Pertanian Baik Malaysia – Dokumen Pegawai*. Jabatan Pertanian Sabah, Kota Kinabalu.

Department of Agriculture Sabah. (2018). *Agricultural Statistics of Sabah*.

Lehotay, S. J., Mastovska, K., & Lightfield, A. (2005). Use of buffering and other means to improve results of problematic pesticides in a fast and easy method for residue analysis of fruits and vegetables. *Journal of AOAC International, 88*(2), 615 - 629.

McLeod H.A. & McCully K.A. (1969). Headspace gas chromatography procedure for screening food samples for dithiocarbamates pesticide residues. *J. AOAC 52*, 1226-1230.

Ministry of Health, Malaysia. (2014). *Food Act 1983 (Act 281) and Regulations*.

Ministry of Health, Malaysia. (2017). *Food Act 1983 (Act 281) and Regulations*.

Ministry of Agriculture and Agro-Based Industry (MOA) Malaysia. (2014). *myGAP Guidelines*. Ministry of Agriculture and Agro-Based Industry (MOA) Malaysia.