Detection of organophosphate pesticide residues of chili (*Capsicum annuum* L.) in different seasons in Aceh province

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Abstract. Chili is one of the essential food products that serve as a flavoring ingredient in the diet of the Indonesian people, especially in Aceh province. The analysis was conducted to investigate the safety level of chili sold in traditional markets of Aceh. The analysis was carried out on chili products sold in two different seasons, the rainy season (February, March and October) and the dry season (April, May, and August). Analysis of chili harvested in the rainy season was carried out on six samples from 6 districts. In comparison, analysis on samples sold in the dry season was obtained from 27 samples from 17 districts within Aceh Province. The study was conducted to analyze the pesticide residue of chili, which was traded in the traditional market in Aceh province for pesticides belong to the organophosphate group. Analysis was performed using Gas Chromatography (GC). The results of the analysis showed that in the rainy season, pesticide residue found in 2 districts (Aceh Besar and Bireuen districts). This residue belong to chlorpyrifos (0.74 mg kg⁻¹) and dimethoate (0.61 mg kg⁻¹). Meanwhile, in the dry season, five samples in four districts detected pesticide residues from the organophosphate group. However, only one district (Aceh Tamiang) had pesticide residues exceeding the MRL or more than 3 mg kg⁻¹. The pesticide residue obtained in Aceh Tamiang district is (5.18 mg kg⁻¹) from the profenofos group.

1. Introduction

Red chili (*Capsicum Peppericum*) is a vital horticulture commodity in Indonesia, especially in Aceh Province. Chili is widely used in daily culinary. The average consumption of red chilies could reach 13.25 kg person⁻¹ year⁻¹. Therefore, Aceh Province needs around 68,000 tons of chili annually. According to Aceh statistics (2019), chili production in Aceh fluctuated from 53,800 tons in 2017, 68,153 tons in 2018, and 63,595 tons in 2019. Moreover, FAOSTAT (2020) shows that China, Mexico, Turkey, Indonesia and Spain have the most significant production quantity and altogether produce approximately 75% of the world's production of fresh chili.
The price of chili is volatile depending on the power of supply and demand. The price ranged between USD 0.75 and 8.33 in the traditional market. Particularly during religious occasions, the demand for chili increased. Although chili could be grown all year round, the market is oversupplied in the dry season. The chili production is low during the rainy season, associated with a high risk of pests and diseases attack [1]. The incidence of abnormal weather variation has been more frequent and rampant recently, brought to the different yields of the chili [2]. Many farmers, especially in Indonesia, try to gain more profit by growing chili in the wet season, although they should use high pesticide intensity.

Farmers rely on chemical pesticides to control pests and diseases because they are more effective and efficient than natural ones [3-5]. Usually, pesticides applied for vegetable crops belong to the group organophosphates such as dimethoate, chlorpyrifos, and cypermethrin. Excessive use of pesticides might be due to the increasing attack of pests and diseases as an impact of increasing temperature due to climate change [6]. They are used excessively and leaving a residue above the allowed level [7]. Herbicide residues have a negative impact on human health, which is estimated to increase the number of cancer cases in humans related to consuming fruits and vegetables containing pesticides residue [8].

Various studies have also shown that pesticide residues in food are associated with various diseases such as hemopoietic disorders or various types of human organ cancer [9,10]. Very little has been carried out on its residues estimation; therefore, the present study was conducted to analyze pesticide residues in chili cultivated by farmers, primarily due to differences in planting or harvesting seasons. This article aims to investigate the safety of fresh chili in Aceh Province, one of Indonesia's chili production areas, and try to find out its relationship with the pesticide practice of local farmers.

2. Material and Methods
2.1 Time of research and sampling procedure
This research was conducted from January to December 2019. Sampling was taken at 33 markets in Aceh Province, 27 locations during the rainy season (October - March), and 6 locations during the dry season (April - September). This 33 location is located within 17 districts of Aceh Province. Figure 1. Then the samples were immediately taken to the Food Safety Laboratory - Aceh Food Service.

2.2 Preparation for sample analysis
The collected samples were stored in a refrigerator with a temperature of 5 °C. These samples were extracted and analyzed within 24 hours after sampling. Based on the analysis procedure, samples were tested against pesticides in the organophosphate group, consisting of diazinon, methidathion, dimethoate, chlorpyrifos, and profenofos AOAC 2007.01 method concerning Pesticide Residues in Food with Acetonitrile Extraction and Partitioning with Magnesium Sulfate [11].

2.3 Extraction of Sample
Fifty grams of the sample were chopped using a food chopper, and fifteen grams of the homogeneous sample were weighed in a 50 ml tube, then the standard mixture was added (spiked). The sample was left to stand for 30 minutes, added with QuECHERS powder containing (6 g MgSO4 and 1.5 g sodium acetate). Enter the Homogenizer ceramic and add 15 mL of solvent 1% acetic acid in acetonitrile. Then the sample was shaken for 2 minutes and centrifuged for 5 minutes at a speed of 4000 rpm. The extract was taken as much as 8 mL and carried out a clean-up process using absorbent (1200 mg MgSO4 + 400 mg PSA + 400 mg GCB) and centrifuged for 2 minutes at a speed of 4000 rpm. Finally, the extraction results were taken to be analyzed using gas chromatography according to [12,13].

2.4 Analytical procedure
The instrument used to analyze pesticide residues was Gas Chromatography (Shimadzu-series 2010 plus model; Kyoto, Japan), equipped with a Flame Photometric Detector (FPD). The analysis was carried out simultaneously on pesticide residues in the organophosphate group (Dimethoate, Diazinon, Chlorpyrifos, Methidathion, and Profenofos). Each residue has been validated on the linearity, precision, accuracy, reproducibility, and detection limit values. A capillary column Rtx-5 (Crossband 5% diphenyl - 95%
dimethyl polysiloxane, Restek, USA) column size 30 m x 0.25 mm, ID x 0.25 µm df, mobile phase: Helium 99.9995% with a flow rate of 1.2 mL/min, detector temperature at 280 °C, injector temperature at 230 °C, splitless mode and injection volume of 1 µL. Processing of the raw chromatogram and data collection was performed using the GC-Solution program (Shimadzu Corporation). The pesticide residue test results were compared with the Maximum Residue Limit (MRL) of pesticides that have been used in Indonesia and the CODEX Alimentarius standard [14].

3. Results and Discussion

3.1 Pesticide residues during the rainy season

Table 1 shows that there are pesticide residues in chili samples taken during the rainy season (February, March and October 2019) in six traditional markets in the Aceh region. 2 of the 6 samples detected organophosphate pesticide residues, namely chlorpyrifos 0.744 mg kg\(^{-1}\) and dimethoate 0.614 mg kg\(^{-1}\), each detected sample was found in the districts of Aceh Besar and Bireuen. The chlorpyrifos detected in Aceh Besar District was above the set BMR of 0.5 mg kg\(^{-1}\), but the dimethoate residue in chili samples in Bireuen District showed a residue lower than the set BMR of 1 mg kg\(^{-1}\) (Table 2).

Some samples did not find pesticide residues, presumably because organophosphate pesticides are resistant to high temperatures and sunlight, especially the ultraviolet spectrum [15,16]. Weather factors such as high temperatures cause pesticides to be degraded [17]. Organophosphate pesticides are pesticides that do not take long to degrade, pesticides that are degraded into the air will decompose due to the influence of temperature, humidity, and sunlight, especially ultraviolet light, organophosphate insecticides are insecticides that are very toxic but can quickly decompose in nature [18].

No pesticide residue was found in the other 4 chili samples, presumably due to washing due to the rainy season and the interval between harvest and arrival at the market and purchased by consumers. There are 2 possibilities for not detecting some pesticide residues, namely, indeed there is no type of pesticide containing the active ingredient being tested; or the active ingredient is no longer present in the harvested vegetables.

Table 1. Data on pesticide residue testing on red chili samples taken at traditional markets in Aceh province during the rainy season

| No | District/Market | Month | Test Standart | Test Result (mg kg\(^{-1}\)) | MRL (mg kg\(^{-1}\)) | Limit Deteksi GC (mg kg\(^{-1}\)) | Method |
|----|-----------------|-------|---------------|----------------------------|-------------------|-------------------------------|--------|
| 1  | Aceh Besar/ Pagi Lambaro Market | February | Klorpirifos | 0.744 | 0.5 | 0.0572 | IK.07.M PRP |
| 2  | Pidie Jaya district / Ulim Market | March | Profenofos | ND | - | 0.0572 | IK.01.M PRP |
| 3  | Bireuen district /Induk Bireuen Market | March | Dimetoat | 0.614 | 1 | 0.0572 | IK.01.M PRP |
| 4  | Lhokseumawe district / Impres Market | March | Dimetoat | ND | - | 0.0572 | IK.01.M PRP |
| 5  | Aceh Timur district /Peureulak Market | March | Methidatio n | ND | - | 0.0572 | IK.01.M PRP |
According to [19], the loss of pesticide residues is caused by several factors, including temperature, humidity, and ultraviolet light. There is a difference in half-life between tropical and non-tropical climate conditions; tropical climate makes the existing half-life shorter [20].

3.2 Pesticide residues during the dry season
Table 3 shows that 5 of the 27 samples in the dry season (April, May, August 2019) detected organophosphate pesticide residues, namely profenofos, acephate and chlorpyrifos. Each sample was found in Aceh Tamiang District (2 samples), Southwest Aceh (1 sample), South Aceh (1 sample), and Bener Meriah (1 sample). Table 3 also shows that 1 out of 5 samples that detected pesticide residues far exceeded the set BMR, namely samples taken at Kuala Simpang Market, Aceh Tamiang district with a prefonofos content of 5.184 mg kg\textsuperscript{-1} while the BMR was set at 3 mg kg\textsuperscript{-1}.

Table 2: Maximum Residue Limits on chili according to Indonesian minister of agriculture regulation no. 53(2018) and Codex Alimentarius for organophosphate groups

| No | Organophosphate Group | Indonesian Minister of Agriculture Regulation No. 53 (MRL; mg kg\textsuperscript{-1}) | CODEX Alimentarius (MRL; mg kg\textsuperscript{-1}) |
|----|-----------------------|-----------------------------------|-------------------------------------|
| 1  | Dimethoate            | 0.5*                              | 0.5*                                |
| 2  | Diazinon              | 0.05*                             | 0.5*                                |
| 3  | Chlorpyrifos          | 2*                                | 2*                                  |
| 4  | Methiaddition         | 0.1**                             | ¬                                   |
| 5  | Profenofos            | 3                                 | 3                                   |
| 6  | Asefat                | 5                                 | 5                                   |

Note: * = MRL of chili, ** = MRL of tomato, ¬ = No Data MRL

Table 3: Data on pesticide residue test results on red chili samples obtained from traditional markets in Aceh province during the dry season

| No | District/Market          | Month | Test Standart | Test Result (mg kg\textsuperscript{-1}) | MRL (mg kg\textsuperscript{-1}) | Limit Deteksi GC | Method  |
|----|--------------------------|-------|---------------|-----------------------------------------|-------------------------------|------------------|---------|
| 1  | Aceh Tamiang district    | April | Profenofos    | 0.754                                    | 3                             | -                | IK.01.MPRP |
|    | / Kuala Simpang Market   |       |               |                                         |                               |                  |         |
| 2  | Aceh Tengah district     | April | Dimethoat     | ND                                      | -                             | 0.0572           | IK.01.MPRP |
|    | / Pagi Jaya Ilang Market |       |               |                                         |                               |                  |         |
| 3  | Gayo Lues district       | April | Dimethoat     | ND                                      | -                             | 0.0572           | IK.01.MPRP |
|    | / Pajak Terpadu Market   |       |               |                                         |                               |                  |         |
| District                  | Market                     | Month | Chemical  | ND | Concentration | Analytical Method | Code |
|--------------------------|----------------------------|-------|-----------|----|---------------|-------------------|------|
| Aceh Tenggara district   | Pajak Pagi Lawe Bulan      | April | Dimetoat  | ND | -             | 0,0572            | IK.01.MPRP |
| Aceh Barat district      | Bina Usaha Market          | April | Methidation | ND | -             | 0,0572            | IK.01.MPRP |
| Nagan Raya district      | Jeuram Market              | April | Methidation | ND | -             | 0,0572            | IK.01.MPRP |
| ABDYA district           | Blang Pidie Market         | April | Ascfat     | 1,240 | 5 | -             | IK.01.MPRP |
| Aceh Selatan district    | Impres Tapaktuan Market    | April | Klorpirifos | 0,422 | 0,5 | -             | IK.01.MPRP |
| Banda Aceh City          | Peunayong Market           | August| Dimetoat  | ND | -             | 0,0433            | IK. M 02  |
| Aceh Besar district      | Pagi Lambaro Market        | May   | Profenofos | ND | -             | 0,272             | IK.01.MPRP |
| Aceh Besar district      | Pagi Lambaro Market        | August| Diazinon  | ND | -             | -                 | IK. M 02  |
| Pidie district           | Pante Tengah Market        | May   | Profenofos | ND | -             | 0,272             | IK.01.MPRP |
| Pidie district           | Pante Tengah Market        | May   | Chlorpyrifos | ND | -             | -                 | IK. M 02  |
| Pidie Jaya district      | Ulim Market                | May   | Profenofos | ND | -             | 0,272             | IK.01.MPRP |
| Pidie Jaya district      | Ulim Market                | August| Profenofos | ND | -             | -                 | IK. M 02  |
| Bireuen district         | Induk Bireuen Market       | May   | Profenofos | ND | -             | 0,272             | IK.01.MPRP |
| Bireuen district         | Induk Bireuen Market       | May   | Methidation | ND | -             | -                 | IK. M 02  |
| Aceh Timur district      | Idi Market                 | April | Chlorpyrifos | ND | -             | -                 | IK. M 02  |
| Aceh Tamiang district    | Kuala Simpang Market       | May   | Profenofos | 5,184 | 3 | -             | IK.01.MPRP |
| Aceh Tamiang district    | Kuala Simpang Market       | August| Diazinon  | ND | -             | -                 | IK. M 02  |
| Bener Meriah district    | Pondok Baru Market         | May   | Profenofos | ND | -             | 0,272             | IK.01.MPRP |
| Bener Meriah district    | Pondok Baru Market         | August| Chlorpyrifos | 0,09 | 0,5 | -             | IK. M 02  |
Based on the results of the analysis of pesticide residues on chilies taken at traditional markets in the Aceh region, both in the dry and rainy seasons, it shows that both seasons have samples that detect pesticide residues, although they have different levels. This difference can occur due to differences in the amount, frequency of pesticide use, and weather at the location of cultivation and post-harvest from the land to the traditional market.

Samples in the dry season in the market had chlorpyrifos residues of 0.422 mg kg\(^{-1}\) and 0.09 mg kg\(^{-1}\), this residue level was lower than the samples detected with chlorpyrifos in the rainy season, namely 0.744 mg kg\(^{-1}\). This is possible because farmers tend to increase the amount and frequency of pesticide application in the rainy season. The feasibility risk of red chili farming in the dry season is higher than that of red chili farming in the rainy season due to increased pest and disease attacks. The value of R-C ratio in the dry season is 1.997 and in the rainy season is 1.789 \[21\]. However, the price of red chili in the market is relatively higher due to less supply compared to demand \[22\].

In addition to high temperature, half-life is also a factor in the degradation of pesticide residues. According to \[23\], the half-life (t\(\text{½}\)) of the pesticide clopirifos in chili is 4.93 days. Another opinion states that, the half-life (t\(\text{½}\)) of chlorpyrifos is 4.01 days, dimethoate 3.61 days, methodtion 2.86 days, diazinon 2.16 days, and profenofos 2.24 days \[24-26\].

### 4. Conclusions

The results of the analysis showed that in the rainy season pesticide residue levels were still below the BMR found in 2 districts (Aceh Besar and Bireuen) namely chlorpyrifos (0.74 mg kg\(^{-1}\)) and dimethoate (0.61 mg kg\(^{-1}\)). Meanwhile, in the dry season, five samples from four districts (Aceh Tamiang, West Aceh, South Aceh, and Bener Meriah) were detected with pesticide residues, but only one sample in Aceh Tamiang district had profenofos pesticide residues of 5.18 mg kg\(^{-1}\) and far exceeded the BMR, namely 3 mg kg\(^{-1}\) (MoA 2018 and CODEX Alimentarius).

### References

[1] Hussain F, Abid M. Pest and diseases of chilli crop in Pakistan: A review. Int J Biol Biotech. 2011;8(2):325–32.

[2] Tawang A, Ahmad TAT, Abdullah Y. Stabilization of upland agriculture under El Nino induced climatic risk: Impact assessment and mitigation measures in Malaysia. CGPRT Centre Works towards Reducing Poverty through Enhancing Sustainable Agriculture in Asia and the Pacific Region. 2001.
[3] Abedi-Lartey M, Dechmann DKN, Wikelski M, Scharf AK, Fahr J. Long-distance seed dispersal by straw-coloured fruit bats varies by season and landscape. Global Ecology and Conservation. 2016;7:12–24.

[4] Sharifzadeh MS, Abdollahzadeh G, Damalas CA, Rezaei R. Farmers’ criteria for pesticide selection and use in the pest control process. Agriculture (Switzerland). 2018;8(2):1–16.

[5] Zhang X, Du X, Hong J, Du Z, Lu X, Wang X. Effects of climate change on the growing season of alpine grassland in Northern Tibet, China. Global Ecology and Conservation. 2020;23:e01126.

[6] Delcour I, Spanoghe P, Uyttendaele M. Literature review: Impact of climate change on pesticide use. Food Research International. 2015;68:7–15.

[7] Latif Y, Sherazi STH, Bhanger MI. Monitoring of pesticide residues in commonly used fruits in Hyderabad Region, Pakistan. American Journal of Analytical Chemistry. 2011;2(08):46.

[8] Valcke M, Bourgault M-H, Rochette L, Normandin L, Samuel O, Belleville D, et al. Human health risk assessment on the consumption of fruits and vegetables containing residual pesticides: A cancer and non-cancer risk/benefit perspective. Environment international. 2017;108:63–74.

[9] George J, Shukla Y. Pesticides and cancer: insights into toxicoproteomic-based findings. Journal of proteomics. 2011;74(12):2713–22.

[10] Lozowski B. Health risk for children and adults consuming apples with pesticide residue. Science of the Total Environment. 2015;502:184–98.

[11] Lehotay SJ. Pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate gas chromatography/mass spectrometry and liquid chromatography/tandem mass spectrometry. Journal of AOAC International. 2007;90(2):485–520.

[12] Anastassiades M, Lehotay SJ, Štajnbaher D, Schenck FJ. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. Journal of AOAC international. 2003;86(2):412–31

[13] Yusuf M, Idroes R, Bakri TK, Satria M, Nufus H, Yuswandi I, et al. Method validation for pesticide multiresidue analysis of pyrethroid on green beans of arabica gayo coffee using gas chromatography-electron capture detector (GC-ECD). In: IOP Conference Series: Earth and Environmental Science. IOP Publishing; 2021. p. 12039.

[14] Commission JFCA. Codex alimentarius. Food & Agriculture Org.; 1992.

[15] Fest, C., Schmidt, K.-J., 1973. General Section, in The Chemistry of Organophosphorus Pesticides. Springer, pp. 20–49.

[16] Matsumura, F., 2012. Toxicology of insecticides. Springer Science & Business Media.

[17] Damalas, C.A., Eleftherohorinos, I.G., 2011. Pesticide exposure, safety issues, and risk assessment indicators. Int. J. Environ. Res. Public Health 8, 1402–1419.

[18] Lad, K.S., Patel, V.C., Parmar, P., 2017. Profile study of organophosphorus poisoning at Valsad: A 2 year study. J. Indian Acad. Forensic Med. 39, 235–238.

[19] Munawar A A and Sabaruddin Z 2021 Fast classification of rice (Oryza sativa) cultivars based on fragrance and environmental origins by means of near infrared spectroscopy IOP Conf. Ser. Earth Environ. Sci. 644 012003

[20] Atmawidjaja, Tjahjono, Rudyanto.2004.Pengaruh Perlakuan Terhadap Kadar Residu Pestisida Metidation Pada Tomat. Available from:URL:http://acta.fa.itb.ac.id.

[21] Ngan CK, Cheah UB, Wan Abdullah WY, Lim KP dan Ismail BS. 2005. Fate of Chlorothalonil, Chlorpyrifos and Profenofos in a Vegetable Farm in cameron Highlands, Malaysia. Water, Air, and Soil Pollution : Focus 5 :p 125-136.

[22] Mediatama, G., 2020. The Rainy Season, Chili Prices Creep Up in Indonesia. [WWW Document]. kontan.co.id. URL https://nasional.kontan.co.id/news season-rainy-price-chili-go-up (accessed 7.31.21).

[23] Rofatin, B., Wijaya, J., 2020. Comparative Study of Feasibility of Red Chili Farming in Different Seasons in Indonesia. Jurnal Agristan 2.

[24] Kusumiyati, Hadiwijaya Y, Putri I E and Munawar A A 2021 Multi-product calibration model for soluble solids and water content quantification in Cucurbitaceae family, using visible/near-infrared spectroscopy Heliyon 7 e07677
[25] Sushil, C.R., Kumari, B., Jaglan, R.S., 2018. Studies on persistence and dissipation behavior of selected pesticides in hot pepper (Capsicum annuum). Int. J. Chem. Stud. 6, 1791–1794.

[26] Fantke, P., Juraske, R., 2013. Variability of Pesticide Dissipation Half-Lives in Plants [WWW Document]. ACS Publications. https://doi.org/10.1021/es303525x.