Study of paraquat dichloride residue in oil palm

L Nurulalia, N Mubin and Dadang

Department of Plant Protection, Faculty of Agriculture, IPB University, Indonesia

Corresponding author email: lianurulalia@apps.ipb.ac.id

Abstract. Paraquat dichloride is a non-selective contact herbicide commonly used in oil palm plantations. It causes the leaves to wilt quickly, dehydrate, and eventually die. The aim of this study was to evaluate the extent of paraquat residues in oil palm fruits. The study has conducted from November 2019 to February 2020. Fruit samples were collected from oil palm plantations in three provinces (North Sumatra, Jambi, and West Kalimantan). Paraquat is applied two times per year with a high volume spraying dose of one liter per hectare. The last application of paraquat dichloride was 30 days before harvest in North Sumatra and Jambi, and 14 days in West Kalimantan. The samples were taken randomly from five trees aged eight years (TM-8), then mixed for analysis. The result showed that paraquat residue content was undetected at the analytical detection limit of 0.0151 ppm. It means that the paraquat residue was below the detection level or that there was no residue in the oil palm fruits. As a result, the application of paraquat to control the weeds around the plantation leaves no residue in oil palm fruits.

Keywords: herbicide, oil palm fruits, weeds control

1. Introduction

Oil palm is a valuable plantation commodity in Indonesia that produces oil for food processing, industrial use, and fuel (biodiesel). One of the activities to maintain the oil palm plantation is weeds control, which is mainly on the disk area (± 1-2 m from the oil palm tree). Weeding is also done in the area among oil palm trees [1]. Weeds are plants that grow among the primary crops, competing for water, nutrients, and light. It occasionally serves as an alternative host for insect pests. As a result, weeds can prevent optimal plant growth, reduce production by up to 80% and the income of the farmers [2]. Some weed control strategies are manual weeding, plowing, and the use of chemical herbicides. Every farmer is free to select the methods that are most suited to their needs. Manual weeding is time-consuming, and farmers with small landholdings may not afford to hire weeding labor [2]. Weed control with herbicides is commonly applied by oil palm farmers in Indonesia [1]. The application of herbicides can reduce the total costs by up to 50% [2]. Synthetic chemical herbicides, such as paraquat, represent a significantly advanced technique in weed management than previous methods [2]. Paraquat is a non-selective contact herbicide that is used for broad-spectrum control of grasses and broad-leaved weeds. It has limited translocation in the xylem after absorption by foliage, resulting in the browning of leaves within a few hours after application. It is a very effective and beneficial method of weed control, and it has become an essential technique in weed management [3]. Farmers also use paraquat to improve harvesting efficiency [1].

However, the importance of food quality and safety has recently become a major concern. The widespread use of pesticides causes problems about the presence of pesticide residues in foods [2]. Pesticide residues are chemicals found in agricultural products directly or indirectly from pesticide
application and have toxicological effects [4]. According to some studies, pesticide residues have been found in a variety of food products. These residues in food have the potential to be hazardous to human health [5]. Therefore, there have been some vocal demands and campaigns to eliminate paraquat and other pesticides. On the other hand, restriction of paraquat use would reduce the incomes and livelihoods of many farmers worldwide [2]. Based on paraquat residue issues, the purpose of this study is to evaluate the presence of paraquat dichloride residue in oil palm fruits as a raw material for crude or refined palm oil, with the result of providing scientific information about the presence of paraquat residues in oil palm after herbicide application.

2. Method

The study was conducted from November 2019 to February 2020. Samples have been taken from three oil palm plantations aged eight years (TM-8). The fruit samples were brought to the Laboratory of Agricultural Environmental Research Institute, Ministry of Agriculture to be analyzed for residual paraquat dichloride levels.

2.1. Sampling locations

The sampling locations are the oil palm plantations that have used the herbicide paraquat dichloride for weed control. Oil palm fruit samples were collected from oil palm plantations in three provinces: North Sumatra (Langkat), Jambi (Tanjung Jabung), and West Kalimantan (Landak). The herbicide paraquat dichloride was applied to their fields 30 days before the oil palm fruit was harvested in North Sumatra and Jambi, and 14 days in West Kalimantan. The samples were fresh fruits harvested directly from the trees. Paraquat is applied two times per year with a high volume spraying dose of one liter per hectare. The plantations had previously been threatened with the herbicide paraquat dichloride at the recommended concentration/dose by the farmer. The samples were taken randomly from five trees. The samples were mixed and weighed to about 1 kg before being placed into a plastic bag. The samples were placed in a cool box and brought to the laboratory.

2.2. Sample extraction and purification

The sample was extracted using QuEChERS (quick, easy, cheap, rugged, and safe) method. Chemical compound extraction from various matrices is a time-consuming procedure. However, the QuEChERS technique reduces the analysis stages (by using fewer reagents in smaller quantities) and achieves high recovery in the process [5]. The QuEChERS method is a multi-residue technique to detect pesticides residues. This method has revealed high accuracy and precision for all pesticides. There are three types of QuEChERS methods: (1) the non-buffer QuEChERS method; (2) the AOAC (Association of Official Analytical Chemist) Official Method (using acetate buffer), and (3) the European Standard Method EN 15662:2008 (using citrate buffer) [6]. The extraction and purification process in this study was based on the AOAC Official Method.

About 0.5 – 1.0 kg fruit samples with ethyl acetate were homogenized using a mixer. A total of 20 g of extracted sample was then placed into a 250 ml Erlenmeyer flask. After that, 150 ml of 0.1 M potassium hydroxide (KOH) was added to each sample, then shaken for 16 hours. After shaking, the sample was heated on a hot plate for 1 minute. The hot Erlenmeyer was then removed and cooled. Next, each sample was centrifuged for 10 minutes at 4000 rpm. The results of the centrifugation were then filtered. The clear extract was collected in a 300 ml round flask. Centrifugation precipitate rinsed with 25 ml of HCl 0.01 M reagent, then centrifuged for 10 minutes. The extract was mixed with the previous extract in a 300 ml round flask. Before being transferred to a centrifuge tube, the mixture was concentrated with a rotary evaporator to a volume of 5 ml under vacuum at 60°C and a pH of 1.8-2.0. Centrifugation was carried out for 10 minutes at a speed of 2500 rpm. After that, the extract was flowed through the cation exchange column and rinsed with 2 x 55 ml of HCl 0.01 M. The mixture was then concentrated again in a rotary evaporator under vacuum at 60°C to volume 5 ml, which was then adjusted to 10 ml with the addition of 70% methanol.
2.3. Paraquat residue determination
The paraquat residue for each sample has been analyzed by HPLC (high-performance liquid chromatography) (Agilent 1260) with a diode array detector and fluorescence detector equipped with a C18 colon (4.6 mm x 150 mm) at a column temperature of 35°C. The mobile phase used 70% methanol at a flow rate of 0.5 ml/minute. The volume of the sample injected was 5 μl. The concentration of paraquat dichloride was determined by comparing the sample peak height to the standard calibration curve. The residual content of paraquat in the sample is determined as the formula follows:

\[ R = \frac{D \times V}{W \times 1000} \text{ (ppm)} \]

Where R is the residual content in the sample (ppm), D is the amount of paraquat detected in the injection volume (nanogram), V is the final volume (ml), I is the injection volume (l), and W is the weight of the sample volume (g).

3. Result
3.1. Paraquat herbicide application
The grasses around the trees that have been sprayed by paraquat herbicide appear brownish and dry (Figure 1). Paraquat herbicide acts in the chloroplast by diverting the flow of electrons from photosystem I (PS I). The interaction of paraquat with the electron transport of PS I reduces the amount of net O₂ and inhibits CO₂ fixation, resulting in the formation of superoxide (O₂⁻) [7]. The superoxide formed will then react with two H⁺ ions to form peroxide acid (H₂O₂). When there is sunlight, peroxide acid will decompose into reactive free radicals, which bind to fat electrons in cell membranes (lipid peroxidation). The result is cell damage to cell death [8]. Therefore, after paraquat application to weeds and weeds are exposed to sunlight, the weeds will immediately show symptoms of poisoning within a few hours.

![Figure 1. Grasses are drying after 14 days of herbicide paraquat application at an oil palm plantation in West Kalimantan.](image)

3.2. Paraquat dichloride residue
This study found that residual of paraquat content in oil palm fruits from three plantations is undetectable at the analytical limit of detection (LoD) of instrument, 0.0151 ppm (mg/kg). According to the results, the residual level of paraquat dichloride in the oil palm fruit samples is less than the pre-defined detection limit, or there is no residue in the fruits. The herbicide paraquat was only sprayed on the disc area and...
the areas between the trees, and was not applied to oil palm trees. If there is herbicide drift, it is usually only a small amount. In this case, the herbicide paraquat does not affect the oil palm fruit directly. According to a study on the assessment of paraquat residues in oil palm in Malaysia, none of the fruit samples had paraquat residues. It explained that using paraquat in oil palm plantations at the recommended dose in compliance with good agricultural practices (GAP) did not result in any residue issues. It also assures that the herbicide was not sprayed directly on the oil palm trees in plantations for weed control [9].

Pesticide residues in agricultural products depend on several factors, including the intensity of application, concentration/dose, mode of action (persistence, systemic/non-systemic), pesticide additives, plant morphology, and the last application of pesticide before harvest (pre-harvest interval/PHI). The combination of these factors will determine the number of pesticide residues in agricultural products [10]. Concerning the timing of the last herbicide paraquat application, the treatment 30 and 14 days before harvesting, the paraquat residue was below the detection limit, or there was no residue in the oil palm fruit. It also provides information that applying the herbicide paraquat at least 14 days before harvest time is still safe for some reasons. Because paraquat dichloride is a non-systemic herbicide, it cannot be translocated to plant tissues and only affects the exposed parts of plants. Non-systemic refers to it not circulating within the plant [3].

Pesticide residue issues are associated with the term maximum residue limit (MRL), which refers to the value or residual content of the pesticide. MRL is the maximum pesticide residue concentration permitted or recognized as an acceptable concentration in agricultural products, stated in milligrams of pesticide residues per kilogram of agricultural products [4]. The Codex Alimentarius Commission (CAC), the European Union Commission (EU), and the Gulf Cooperation Council (GCC) are in charge of the MRL in fifty countries, with twenty-three following their own set of MRL [5]. Even though paraquat dichloride has been used in Indonesia since the 1960s, it is not included the regulated list in the Joint Decree of the Minister of Health and the Minister of Agriculture No. 881/MENKES/SKB/VIII/1996 concerning the maximum limit of pesticide residues in agricultural products [11]. Meanwhile, the Indonesian National Standard (SNI) No. 7313:2008 [4] and the FAO-WHO Codex Alimentarius (CA) [12] set the maximum limit for paraquat residues in agricultural products, such as rice, maize, soybean, potato, sorghum, sunflower seed, cottonseed, passion fruits, citrus fruits, leafy and fruiting vegetables, root and tuber vegetables, and tea. The MRL value for plantation commodities, such as oil palm, is not included in SNI or CA. As a result, the authorities must determine the MRL for paraquat in plantation commodities in the future.

**Table 1.** The MRLs value of sunflower and cottonseed (as a comparison to oil palm) according to SNI and Codex Alimentarius (CA).

| No | Commodity                  | MRLs value (ppm)                          |
|----|----------------------------|------------------------------------------|
|    |                            | **Codex Alimentarius** | **SNI** |
| 1  | Sunflower seed             | 2                                        | 2       |
| 2  | Sunflower seed oil (edible)| 0.05                                     | 0.05    |
| 3  | Sunflower seed oil (crude) | 0.05                                     | 0.05    |
| 4  | Cottonseed                | 2                                        | 0.2     |
| 5  | Cottonseed oil (edible)   | 0.05                                     | 0.05    |
| 6  | Cottonseed oil (crude)    | -                                        | 0.05    |

Oil palm fruits are processed into crude or refined oil products. As a comparison, the MRL value for sunflower seed and cottonseed, which are also processed into oil products, can be seen in Table 1. The MRL value for sunflower seed and cottonseed is at a range value of 0.2 to 2 ppm, while the MRL value for those oils is 0.05 ppm. The paraquat residue in oil palm fruit is found to be less than 0.0151 ppm. As
a result, it remains far below the MRL value established by CA and SNI. The WHO established MRL to ensure that food is safe for human consumption. Most of the existing MRLs for paraquat in raw agricultural commodities are set at 0.05 ppm. These MRLs are derived from herbicide application at pre-plant, pre-emergence, and crops inter-row [13].

4. Discussion
Paraquat is a contact herbicide that is not translocated in plant tissues. The exposure of herbicide in plants is still possible to leave residues in small amounts. However, residues on the leaves will naturally degrade through a photochemical process rather than through metabolic processes [14]. A study on the rice field at Cikampek, West Java, found no residue in grains and rice straws with the application of paraquat herbicide at a recommended dose. Meanwhile, on a high-dose herbicide application, the paraquat residue found was in a small number, around 0.001 ppm [10]. This result was less than the Codex MRL of 0.05 ppm [12]. Because paraquat on the surface of a plant can be degraded by sunlight, the paraquat content is rarely found in foods. Paraquat that falls to the ground is rapidly and strongly absorbed by clay particles in the soil and thus is not absorbed by plants. In the soil, paraquat herbicide can be degraded by microorganisms such as fungi and bacteria [2].

Although pesticides are used extensively nowadays, pests and weeds problem still cause crop losses of up to almost half of the food crops in the world. A synthetic chemical herbicide, like paraquat, represents a significant technological advance in weed management over earlier technologies, such as manual weeding, mechanical weeding, and arsenic-based herbicide application. Weeding by hand and by machine is more time-consuming and more expensive. In weed control, the major problem that needs to be handled is related to weed resistance to particular herbicides. However, after over 40 years of usage, the paraquat formulations remain effective against weeds and have become part of integrated pest management methods in many countries [2].

Many countries have evaluated the herbicide paraquat, particularly in terms of safety and environmental health. Some countries even have prohibited the use of paraquat in their authority for various reasons. Some of them restrict paraquat because it has high acute toxicity and a high risk of accidents during handling and its usage. Another reason is that the herbicide paraquat is often used to commit suicide in some countries. The reasons for the prohibition of paraquat derived from a hazard-based decision and risk estimations rather than scientific-technical reasons and actual incidents in actual use in the field. However, there are also some countries, including Indonesia, that only restrict paraquat on its usage. In Indonesia, paraquat herbicide can be used by people or farmers who have received training in using this herbicide. This is to avoid accidents when applying paraquat herbicide in the field. The requirement for this training has been regulated by the Ministry of Agriculture regarding the regulation of pesticide registration [10].

Herbicides have become one of the production inputs required in oil palm plantations in Indonesia, mainly to increase production and agricultural productivity. Farmers want herbicides that are of high quality, sufficient quantity, and reasonably priced. The demand for herbicide production is influenced by several factors, including weed control efficacy and prices. In addition, the price of CPO (crude palm oil) also affects the demand for herbicides. An increase in CPO prices will encourage farmers to increase their oil palm production [10]. Paraquat herbicide has played an important role in improving agricultural efficiency. This success story has generated both positive and negative publicity. One of the factors supporting the success of oil palm plantations is the effectiveness of herbicides, specifically paraquat, in controlling weeds that can reduce oil palm productivity [2]. The herbicide paraquat has become an essential input in oil palm production. Paraquat is considered to be one of the most effective tools in weed management. This indicates that paraquat has an important role in oil palm cultivation in Indonesia [5]. Therefore, many paraquat studies must continue to be conducted, such as environmental security, work safety, and technical and economic issues, to maintain the sustainability of oil palm plantations in Indonesia.
5. Conclusion
The residual level of paraquat dichloride in oil palm fruits was less than the detection limit (LoD < 0.0151 ppm), indicating that the residue of paraquat in the oil palm fruits is very low (undetectable). The herbicide paraquat application at dose of one liter per hectare to the weeds around the oil palm trees does not leave a residue in the oil palm fruits of eight-year-old trees (TM-8). Paraquat herbicide belongs to the category of limited pesticides in Indonesia. The application of herbicide paraquat must consider the environmental and work safety aspects for the sustainability of oil palm cultivation in Indonesia.

Acknowledgments
The authors are giving appreciation to the oil palm farmers at the sampling locations, PT. Syngenta Indonesia for financial and technical support, and the Laboratory within the Ministry of Agriculture for assisting in the residue analysis.

References
[1] Balai Pengkajian Teknologi Pertanian (BPTP) 2008 Teknologi Budidaya Kelapa Sawit Badan Penelitian dan Pengembangan Pertanian Lampung: Kementerian Pertanian Bhttp://lampung.litbang.pertanian.go.id/ind/images/stories/publikasi/sawit.pdf
[2] Srinivasan P 2004 Paraquat, a unique contributor to agriculture and sustainable development https://conservationagriculture.org/app/uploads/2019/02/CASE-FOR-PARAQUAT-SRINIVASAN-2003.pdf.
[3] Rutherford M, and Sastrountomo S S 2011 Rountable for sustainable palm oil (RSPO) research project on integrated weed management strategies for oil palm. Final Report https://www.rspo.org/file/RSPO%20IWM_FINAL%20REPORT%20to%20RSPO%2009%205%202011.pdf
[4] Standar Nasional Indonesia (SNI) 2008 SNI 7313: Batas Maksimum Residu Pestisida pada Hasil Pertanian. Badan Standardisasi Nasional (BSN) http://www.chilealimentosinodato.cl/uploads/rules/indonesia-batas-maksimum-pestisida.pdf%3Fv1.6
[5] Narenderan S T, Meyyanathan S N, and Babu B 2020 Review of pesticide residue analysis in vegetables: pre-treatment, extraction and detection techniques Food Research International - Elsevier 133(2020)109141 https://doi.org/10.1016/j.foodres.2020.109141
[6] Oshita D, and Jardim I C S F 2014 Evaluation of dispersive and cartridge SPE clean-up procedures using the modified QuEChERs method for the analysis of pesticides in strawberries Royal Society of Chemistry - Analytical Methods https://10.1039/c4ay01867b
[7] Ananieva E A, Christov K N, and Popova L P 2004 Exogenous treatment with salicylic acid leads to increased antioxidant capacity in leaves of barley plants exposed to paraquat. J. Plant Physiol. 161 3 319-328 https://doi.org/10.1078/0176-1617-01022
[8] Smith L L 1985 Paraquat toxicity Philosophical Transactions of the Royal Society B: Biological Sciences 311 1152 647-657 https://doi:10.1098/rstb.1985.0170
[9] Halim N, Kunto M, Shinde R, and Banerjee K 2019 Determination of paraquat residues in palm oil by high-performance liquid chromatography with uv and tandem mass spectrometry European Journal of Lipid Science and Technology https://10.1002/ejlt.201900092
[10] Dadang, Kurniadi D, Suryani N, Budianto, Ardiwinita A N, Hakim D B, Tjitrosemito S, Purba E, Andayani L S, and Perdana T 2020 Profil Kemanan dan Penggunaan Herbisida Parakuat Diklorida di Indonesia (Bogor: IPB Press) p 93-100
[11] Surat Keputusan Bersama Menteri Kesehatan dan Menteri Pertanian 1996 SKB Menkes dan Mentan, No. 881/MENKES/SKB/VIII/1996 Batas Maksimum Residu Pestisida pada Hasil Pertanian http://perundangan.pertanian.go.id/admin/km_terkait/KepmenTerkait-711-96.pdf
[12] Codex Alimentarius 2021 International food standards (Food and Agriculture Organization (FAO) & World Health Organization (WHO)) http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticide-detail/en/?p_id=57
[13] International Programme on Chemical Safety (IPCS) 1981 Pesticide Residues in Food: Evaluations 1981 (Internationally Peer Reviewed Chemical Safety Information: FAO-WHO) http://www.inchem.org/documents/jmpr/jmpmono/v81pr22.htm
[14] Slade P 1966 *The Fate of Paraquat Applied to Plants* https://onlinelibrary.wiley.com/doi/pdf