Identification of organochlorine insecticide contamination on shallots land in Nganjuk Regency, East Java Province, Indonesia

Indratin, S Wahyuni, Poniman and M T Sutriadi
Indonesian Agricultural Environment Research Institute, Pati, Indonesia
E-mail: indratin.99@gmail.com

Abstract. The high and excessive use of pesticides is reported to have contamination shallot agriculture in Nganjuk Regency, East Java Province, Indonesia. Information on the presence of organochlorine residues needs to be carried out in the context of controlling environmental contamination as a form of implementing a national food security and security program. The purpose of this study was to identify organochlorine residues in shallot land in Nganjuk Regency. Soil samples from the field were taken in March 2020. Soil samples were taken at random diagonally on a stretch of shallot agriculture. Each overlay represents a sampling point. Organochlorine residue analysis was carried out at the Integrated Laboratory, Indonesian Agricultural Environment Research Institute (IAERI) using the QuEChERS method. The results showed that the residual of the organochlorine active ingredient of Endosulfan reaches 0.1066 to 0.1646 mg kg\(^{-1}\), Dieldrin reaches 0.181 mg kg\(^{-1}\) and Endrin reaches 0.2249 mg kg\(^{-1}\). These residual numbers have exceeded the MRLs requirements approximately 0.0085 mg kg\(^{-1}\) (Endosulfan), 0.00290 mg kg\(^{-1}\) (Dieldrin) and 0.0075 mg kg\(^{-1}\) (Endrin). These results showed that polluted agricultural land need to get priority on land remediation for sustainable agriculture.

1. Introduction
The use of pesticides in agricultural land management has resulted in increased environmental pollution by man-made chemicals. Among the sources of these pollutants, one of them is organic pollutants such as organochlorines. Organochlorines are included in the class of pesticides that are effective against pests, but have many negative impacts on the environment. Persistent organochlorines can be classified as persistent organic pollutants (POPs) which have characteristics that are difficult to degrade and have high solubility in fat, and can accumulate in animal tissue in a process called bioconcentration.

Ramadhani and Oginawati [1] in Wahyuni [2] reported that organochlorines are classified as Persistent Organic Pollutants (POPs), namely chemical compounds that are persistent in the environment, that are able to bio-accumulate in the food chain, and have a negative impact on human health and the agricultural environment. POPs is known to last longer on the environment since it has a long half-life [4]. Moreover, organochlorine is not water-soluble, but able to dissolve in fats. Since, it is fat-soluble (lipophilicity), it is more possible for bioaccumulation to happen in living things [5-6]. Thus, cancer, genetic and teratogenic mutations, damage to the immune system and endocrine system can be caused by organochlorine insecticides [6-7]. Therefore, to keep the negative impacts from
happening, it is important to take action in advance by identifying the presence of Organochlorine insecticides on human health, aquatic organisms, and more importantly on the environment in general [8–10]. Organochlorines is a group of Persistent Organic Pollutants (POPs) which can cause bioaccumulation in the food chain so that they are harmful to health. Its persistent nature is not easily broken down and has chronic effects, this is harmful to humans and the environment because it can damage the nervous system and disrupt the endocrine system which causes damage to the reproductive nerves [11-12]. Intensive use of pesticides in vegetable cultivation can negatively impact the biotic and physical environment, and harm human health.

The use of chemical pesticides can have a negative impact on the environment due to the presence of pesticide residues left in the soil such as poisoning non-target organisms, polluting water sources, entering the food chain so that they can poison consumers [3]. In the vegetable field, insecticide residues were found in the organochlorine class [1].

Chemical pesticides tend to be uncontrolled in their use. This can be seen as not good in terms of yield quality as well as the environment. However, it is not easy for farmers to avoid applying these methods. Because until now there has been no effective way of managing pests and plant diseases compared to the existing methods. The use of chemical pesticides is still believed to be a powerful way to reduce the risk of pest and disease attacks [13].

The emergence of pesticide residue contamination is caused by the continuous use of pesticides and ignoring compliance with dosage use, as well as the use of pesticides outside official supervision [14]. The uncontrolled use of pesticides will cause various health problems and environmental pollute and over time it will increase the residue left behind agricultural land where pesticides are used. The more intensive use of pesticides at the farmer level causes high pesticide residues on crops, soil, water and also users/farmers [15].

Indratin et al. [16] reported that the blood of vegetable farmers in Pati, Magelang, and Brebes Districts was detected to contain insecticide residues in the organochlorine class, and the highest residual values reached 0.7732 mL L⁻¹ (lindan), 0.1260 mg L⁻¹ (aldrin), 0.0480 mL L⁻¹ (heptachlor), and 0.1493 mL L⁻¹ (endosulfan), respectively. There were 51 farmers whose blood samples were taken, and 100% of the farmers' blood was contaminated with organochlorine residues of lindan and aldrin [16]. The research objective was to identify organochlorine contaminations in the shallot lands of Nganjuk Regency, East Java, Indonesia.

2. Materials and methods
The field research was carried out in Nganjuk Regency, East Java and the samples were analyzed in the Integrated Laboratory of the Indonesian Agricultural Environment Research Institute (IAERI). This activity took place from January to May 2020.

The use of pesticide data was collected by a survey method, farmer interviews in field sampling. Soil samples were taken from the field in 14 sampling points located in 5 districts in Nganjuk. One sampling point consists of 5 individual samples (sub samples), with a distance of 25 to 50 m for each sub-sample in the field. The tool used for taking the sub-soil samples is a soil drill, which is taken from the processing layer with a depth of 20 cm. The individual samples are put in a bucket and mixed until they are homogeneous, then taken as a composite weighing 0.5 to 1 kg, then taken to the laboratory to be analysed for the content of pesticide residues in the soil.

The analysis of pesticide residues used the QuEChERS method. This method is the newest method developed to analyze the residual content of pesticides in a sample. This method prioritizes the analysis principle that is Quick, Easy, Cheap, Effective, Rugged, and Safe. The procedure extraction is done by weighing the soil as much as 10 g, then put it into a Teflon bottle or glass bottle, then add 10 mL of acetone p.a (pro analyse) or you can also use acetonitrile p.a. The solution was shaken for one minute until it was homogeneous, then added 4 g of MgSO₄ powder or could be replaced with NaSO₄ and 1 g of NaCl. The solution was then centrifuged for 2 minutes at a speed of 3,000 rpm. The result is filtered with filter paper coated with anhydrous MgSO₄ or NaSO₄ powder, the extractant reservoir is in
a 10 mL volume scale test tube. Rinse the filter paper with acetone p.a until the volume of the extractant reaches 5 mL then injected into the GC instrument for organochlorine analysis [17].

The calculation process of samples that contained insecticide residue was done by using the formula from the Pesticides Commission [18] and later to be analysed:

\[
\text{Residue (ppm)} = A \times \frac{C}{B} \times \frac{D}{E} \times \frac{F}{G}
\]

Information:
A = concentration of standard solution (µg mL\(^{-1}\))
B = standard peak area (reading data from GC)
C = sample peak area (reading data from GC)
D = volume of standard injected solution (µL)
E = volume of sample injected solution (µL)
F = volume of dilution (mL)
G = initial weight of sample (g)

### 3. Results and discussion

**3.1. Location of soil sampling**

Nganjuk is the second shallot planting center in Java Island. The data from the Food Crops and Horticulture Agriculture Office of Nganjuk Regency, there are 4 sub-districts which are shallot centers, namely Rejoso, Gondang, Sukomoro, Kersono districts. The average land ownership for farmers is 0.25 ha, and 100% of landowners depend on shallots for their livelihoods.

Soil sampling was carried out at 14 sampling points of shallot land consisting of 5 sub-districts, namely (1) Rejoso, (2) Gondang, (3) Sukomoro, (4) Kersono and (5) Tanjunganom. The determination of the point based on information on shallot centers from the agriculture department and based on direct observations in the field. Soil sampling location data is presented in Table 1.

**Table 1. Location of soil sampling in shallot lands in Nganjuk Regency, Indonesia.**

| No. | Village   | Sub-district | Coordinate        |
|-----|-----------|--------------|-------------------|
| 1   | Sukorejo  | Rejoso       | -7°33'49" ; 111°52'59" |
| 2   | Sukorejo  | Rejoso       | -7°33'50" ; 111°53'08" |
| 3   | Mojorembun| Rejoso       | -7°32'54" ; 111°52'20" |
| 4   | Mojorembun| Rejoso       | -7°32'53" ; 111°52'20" |
| 5   | Sidokare  | Rejoso       | -7°33'11" ; 111°52'16" |
| 6   | Sidokare  | Rejoso       | -7°33'45" ; 111°52'10" |
| 7   | Nglingo   | Gondang      | -7°33'15" ; 111°57'55" |
| 8   | Nglingo   | Gondang      | -7°34'16" ; 111°58'12" |
| 9   | Nglingo   | Gondang      | -7°34'16" ; 111°58'12" |
| 10  | Nglinggo  | Gondang      | -7°34'57" ; 111°58'43" |
| 11  | Sukomoro  | Sukomoro     | -7°35'59" ; 111°56'52" |
| 12  | Kapas     | Sukomoro     | -7°36'24" ; 111°55'52" |
| 13  | Kliner, Pelem | Kersono  | -7°36'19" ; 112°04'58" |
| 14  | Sambirejo | Tanjunganom  | -7°36'24" ; 111°55'52" |
3.2. The use of pesticides
The result of the interview survey with farmers showed that pesticide application was carried out by mixing 4-7 kinds. The main reason is the efficiency of time and labor wages. Of the 14 respondents, 6 people (43%) mixed 5 kinds of pesticides, 5 people (36%) mixed 6 kinds of pesticides, 2 people (14%) mixed 7 kinds of pesticides and only 1 person (7%) mixed 4 kinds of pesticides. This is presented in figure 1.

From the interview results with the farmers, there are at least 4 types of pesticides used, this indicates that the use of pesticides on shallot lands is quite high. There are even up to 7 kinds of pesticides in one application.

The spraying dose from interviews with farmers was 14 people while in the field, the majority of the pesticides used were above average. Farmers spraying according to the recommended dose is 14%, 2 times the recommended dose is 36%, 3 times the recommended dose is 29% and uses 21% of the origin of pouring. This is presented in figure 2.
3.3. Pesticide residues on agricultural land

Agricultural land of Nganjuk Regency, from 14 soil sampling points, 4 points of organochlorine pesticides were detected, which are presented in Table 2. The results of the analysis of the highest Organochlorine insecticides were detected in Nglinggo Village, Gondang Sub-district, Nganjuk Regency, East Java, Dieldrin residue of 0.1181 ppm with MRLs (0.0110 ppm) and 0.2249 ppm Endrin residue (MRLs 0.0075 ppm). This shows that the shallot land in Nglinggo Village, Gondang Sub-district, Nganjuk Regency is already above the maximum residue limit (MRLs), so that the land needs to be remediated so that the contamination drops. High contamination in the soil will later be absorbed by plants, and will also affect the quality of the products produced.

| No | Village, Sub District      | Aldrin | Lindan | Endosulfan | Heptaklor | Dieldrin | Endrin | DDT |
|----|----------------------------|--------|--------|------------|-----------|----------|--------|-----|
| 1  | Sukorejo, Rejoso           | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 2  | Mojorembun, Rejoso         | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 3  | Sidokare, Rejoso           | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 4  | Nglinggo, Gondang          | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 5  | Nglinggo, Gondang          | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 6  | Sukomoro, Sukomoro         | <LoD   | <LoD   | 0.1066     | <LoD      | <LoD     | <LoD   | <LoD|
| 7  | Sukorejo, Rejoso           | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 8  | Mojorembun, Rejoso         | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 9  | Sidokare, Rejoso           | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 10 | Nglinggo, Gondang          | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 11 | Nglinggo, Gondang          | <LoD   | <LoD   | 0.1085     | <LoD      | 0.1181   | <LoD   | <LoD|
| 12 | Kapas, Sukomoro            | <LoD   | <LoD   | 0.1646     | <LoD      | <LoD     | <LoD   | <LoD|
| 13 | Pelem-Kersono              | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|
| 14 | Sambirejo, Tanjungananom   | <LoD   | <LoD   | <LoD       | <LoD      | <LoD     | <LoD   | <LoD|

Limit of Detection (LoD) 0.0029 0.0024 0.0021 0.0024 0.0042 0.0045 0.0039
Maksimum Residue Limits (MRLs) 0.0290* 0.01 0.0085 0.0390** 0.0290** 0.0075** 0.0150**

Source: IAERI’s Integrated laboratory analysis result, 2020.
*Env. Man.Act Cont. Sit. Reg, 2009.
** Alberta Environment and Park, 2019 [19].
LoD: value is the ability of the GC tool to detect the lowest value that can be read by the GC tool.

Based on the data from the analysis of pesticide residues, it shows that the land of Nganjuk Regency is an ecological system that is partially contaminated with organochlorines, even at some points detected above the BMR, namely in Sukomoro Village, Sukomoro District, Nglinggo Village, Gondang District, Palem Village, Kersono District.

4. Conclusions

From the results of the study it can be concluded that the identification results of organochlorine contaminants at various locations in Nganjuk Regency found Endosulfan residues between <LoD to 0.1646 ppm, residual dieldrin between <LoD to 0.1181 ppm and Endrin residue between <LoD to 0.2249 ppm. Endosulfan residues were identified at three sampling points, dieldrin and endrin residues were identified as one sampling point that exceeded MRLs, meaning that high contaminants were
identified. Land remediation is needed to reduce pollution. Those whose value is less than LoD does not mean that it is not polluted, it can be polluted, but the value is still very low, even though it also needs attention to realize sustainable agriculture.

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