Distribution of endosulfan insecticide residues on intensive shallot agriculture farming in Brebes Regency, Indonesia

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Abstract. Endosulfan is an insecticide from the organochlorine group which was last banned in Indonesia in 2013. Endosulfan is very effective in controlling for organisms pest management and is widely used, including for controlling pest of shallot plants. The objective of the research to determine the distribution of endosulfan residues that has been carried out in three villages representing intensive shallot planting areas in Brebes Regency. The three villages were Wanasari, Siasem, and Pebatan in Wanasari sub-District. Soil sampling was carried out in June-July 2019. The prediction area of the residual endosulfan distribution in the research was 1,853 ha. The analysis of endosulfan residues was carried out in the integrated laboratory of the Indonesian Agricultural Environment Research Institute, using the QuEChERS method. From 14 soil sampling points, eleven of them were detected containing endosulfan residues exceeding Maximum Residues Limit (MRLs) of 0.0085 mg kg\textsuperscript{-1}. The distribution of endosulfan residues was mapping using the spline interpolation method and divided into five categories very low, low, medium, high, very high. Interpolation showed 68.47\% of the land experienced very high endosulfan residual pollution (>0.0117 mg kg\textsuperscript{-1}). These results showed that pollute agricultural land need to get priority on land remediation for sustainable agriculture.

1. Introduction

As a member country of the World Trade Organization (WTO), Indonesia has an interest in protecting trade commodities; while as a country that has ratified the Stockholm convention, Indonesia must actively take courage in zero waste. Each trade product is required to be free from chemical contamination that has the potential to harm the health of consumers. Since 2017, Indonesia's exports of shallots abroad in 2017 reached 6,588,605 kg \cite{1}. Shallot cultivation is highly dependent on the use of chemical insecticides to control plant pests. The intensity of insecticide usage on shallot plants is very high and is believed to be a powerful way to reduce the risk of pest infestation. In normal situations, insecticides on shallot plants are applied once every three days, while in severe pest conditions; insecticide applications are applied every other day.

The level of shallot production in Brebes Regency plays an important role in the national shallot stock. The stock national shallot is highly influenced by the success of the shallot harvest in Brebes regency. The lack management of pests and disease will affect the production of shallot then reducing farmer income. Pest and disease management in shallot plants cannot be separated from the use of artificial insecticides that is widely used by shallot farmers in Brebes. It is believed that endosulfan in
insecticide can control the pests of silkworms and armyworms and often used by shallot farmers until 2015. Apart from being easy to obtain and inexpensive, this insecticide is very effective in controlling pests in various crops including shallots. Endosulfan is very toxic to the environment and also to living things. Endosulfan is easily found in almost the earth’s entire surface [2]. In meat and freshwater pond water, endosulfan residues were found [3]. Endosulfan contamination is also found in the air in the agricultural area of the upstream area of the Citarum River [4].

Endosulfan residues were found in intensive agricultural land in India [5]. Endosulfan residue can be found in various agricultural products. Residues of Endosulfan were found in carrots from Malang and Cianjur [6] and in leaf vegetables [7]. Ahn et al. [8] reported the presence of endosulfan residues in fruit and root vegetables. Endosulfan insecticide residues were found in vegetable products from the Dieng highlands [9] and vegetables from Magelang [10]. Endosulfan residues were found in rice [7,11]. Acute exposure to Endosulfan in humans can cause seizures, psychiatric disorders, epilepsy, paralysis, brain endema, memory problems, and death, while chronic exposure can result in immune suppression, neurological disorders, and congenital birth defects [11].

Due to the level of danger posed by Endosulfan, this insecticide was banned under the Stockholm Convention in April 2011. Indonesia has banned the circulation of Endosulfan in stages since 2013 and has been permanently banned since 2015 Now endosulfan has been no longer used since 2015 [12].

Information on the distribution of endosulfan residues is very important to support the export documents for shallot products in Brebes Regency. Insecticide residue contamination comes from the soil or is directly exposed during application. The objective of the research was to determine the distribution of endosulfan residues that has been carried out in three villages representing intensive shallot planting areas in Brebes Regency.

2. Materials and methods

2.1. Sampling method

Soil samples were taken at a depth of 0 to 20 cm, with a stainless-steel soil auger. Each coordinate sampling point was taken as many as 5 to 7 sub-sample points, then from the sub-points were mixed in a large bucket of 10 kg volume, then taken as much as 0.5 kg and contained plastic to be brought under to the laboratory for analysis of OCPs insecticide residues. Each plastic must be given a sample identity label such as Sample number, coordinates, date of collection. Every coordinate point is recorded with its coordinates with the help of GPS MAP 78S type. The coordinates and village administrative areas in Brebes Regency, Central Java, Indonesia are presented in table 1.

| No | Latitude   | Longitude  | Government administration (Village) |
|----|------------|------------|-------------------------------------|
| 1  | 06° 52' 631" | 109° 03' 522" | Wanasari                             |
| 2  | 06° 53' 348" | 109° 01' 261" | Siasem                               |
| 3  | 06° 53' 202" | 109° 01' 283" | Pebatan                              |
| 4  | 06° 52' 671" | 109° 01' 307" | Siasem                               |
| 5  | 06° 52' 944" | 109° 01' 276" | Wanasari                             |
| 6  | 06° 53' 408" | 109° 01' 423" | Pebatan                              |
| 7  | 06° 52' 817" | 109° 01' 459" | Pebatan                              |
| 8  | 06° 52' 718" | 109° 01' 391" | Pebatan                              |
| 9  | 06° 52' 533" | 109° 01' 390" | Pebatan                              |
| 10 | 06° 52' 486" | 109° 01' 484" | Pebatan                              |
| 11 | 06° 52' 319" | 109° 01' 483" | Pebatan                              |
| 12 | 06° 52' 255" | 109° 01' 566" | Siasem                               |
| 13 | 06° 53' 308" | 109° 00' 263" | Siasem                               |
| 14 | 06° 53' 308" | 109° 01' 276" | Wanasari                             |
2.2. Analysis of endosulfan residue in the laboratory

Analysis of endosulfan residue was carried out at the Integrated Laboratory of the Indonesian Institute for Agricultural Research (Accreditation of Testing Laboratory Number: LP-556-IDN). The analysis of Endosulfan insecticide is based on SNI 06-6991.1-2004 method. QuEChERS method was used to soil extraction for determining the pesticide residues [13]. 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 analysis) or you can also use acetonitrile p.a. The solution was shaken for one minute until it was homogeneous, then added 4 g of MgSO$_4$ powder or could be replaced with NaSO$_4$ 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 MgSO$_4$ or NaSO$_4$ 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 [13].

The calculation of insecticide residue content in the sample was based on the formula from the Pesticides Commission [14] and the data were analyzed descriptively:

$$\text{Residu (ppm)} = \frac{A 	imes C 	imes D 	imes E}{B 	imes F 	imes G}$$

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

2.3. Mapping the distribution residues of endosulfan insecticides

In mapping the endosulfan residues distribution, ArcGIS software series 10.4 with a map scale of 1:30,000 was used. The distribution of endosulfan residues was mapping using the spline interpolation method and divided into five categories very low, low, medium, high, very high. Determining the magnitude of the range of values is done by subtracting the value of MRLs-LoD divided by two for each active ingredient. The amount of MRLs according to [15] is 0.0085 mg kg$^{-1}$ for endosulfan.

Moreover, spline interpolation can also be used to calculate values using mathematical functions and can minimize the curvature that connects the values of the observed sample point [16]. Using ArcGIS spline interpolation helped the mapping process to be done [17]. In addition, geospatial is also able to provide an overview of each observation and can be associated with the extent of the impact caused [18–21].

3. Results and discussion

3.1. Endosulfan residue concentration in shallot lands

Soil samples were taken from three villages, namely Wanasari, Siasem and Pebatan Villages, Wanasari Sub-district, Brebes Regency, Central Java Province. There has been found 11 sampling points out of 14 sampling points in which the soil was tested for endosulfan residue that the concentrations were above the BMR value. The residual endosulfan concentrations are presented in table 2.
Table 2. Endosulfan insecticide residues in the shallot lands in Wanasari Sub-district 2019.

| Location | Endosulfan residue | Information                  |
|----------|--------------------|------------------------------|
| 1        | 0.0293             | MRLs = 0.0085 mg kg⁻¹ [18]   |
| 2        | 0.0186             | LoD value = 0.0021           |
| 3        | 0.0257             |                              |
| 4        | 0.0194             |                              |
| 5        | 0.0209             |                              |
| 6        | 0.0202             |                              |
| 7        | 0.0334             |                              |
| 8        | 0.1199             |                              |
| 9        | 0.1145             |                              |
| 10       | 0.1291             |                              |
| 11       | 0.0407             |                              |
| 12       | <LoD               |                              |
| 13       | <LoD               |                              |
| 14       | <LoD               |                              |

The maximum residue limits of endosulfan residues in the soil is 0.0085 mg kg⁻¹ [18]. The test results in the laboratory identified 11 samples whose values exceeded the MRLs ranging from 0.0186-0.1199 mg kg⁻¹ (MRLs value = 0.085 mg kg⁻¹).

3.2. The distribution residues of endosulfan insecticides

The results of these residual figures and after the residual distribution map was made, the area of each category was obtained. The highest to lowest areas were in the very high (1,268.8 ha), high (78.479 ha), medium (82.169 ha), and very low (75.786 ha) categories, respectively. The endosulfan residue distribution map is presented in figure 1.

The half-life of endosulfan in the soil takes 60 to 800 days [22]. Although mathematically, the half-life has expired since it was banned from use in Indonesia, the residue is still easy to find. This is from the nature of the endosulfan itself which is persistent. Endosulfan is easily biodegradable. However, endosulfan is also easily bioaccumulated in the soil by certain microbes [23-24]. This is why endosulfan is still easily found in agricultural lands.

The research locations were shallot cultivation, where the use of insecticides was confirmed to be intensive. The previous research has proven that almost all vegetable crops are intensive in the use of insecticides, such as carrots and cabbage in Wonosobo [13], in Magelang [14].

Similar information was also reported by overseas researchers. Kim et al. [25] reported the distribution of endosulfan residues in soil, water, sediment and air in South Korea. Even endosulfan is also distributed in very remote locations where endosulfan is never used. Endosulfan was discovered by Weber [16] at the North Pole. Kuman et al. [17] have identified insecticide residues of endosulfan and other organochlorines in agricultural, coastal, and coastal areas in India.
Figure 1. Distribution of residue endosulfan in Wanasari Sub district Brebes Regency, 2019.

4. Conclusions
The distribution of endosulfan residue in three villages namely Wanasari, Siasem, and Pebatan is very varied. The highest to lowest areas were in the very high (1,268.8 ha), high (78,479 ha), medium (82,169 ha), and very low (75,786 ha) categories, respectively.

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