Information on the Distribution of Cadmium in Agricultural Land in the Middle of the Serayu Watershed

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Abstract
Cadmium (Cd) is a heavy metal that is prohibited in food products. In the long term, consumption of food containing Cd can cause cancer (it is a direct carcinogen in humans). Poor management of the Serayu watershed has resulted in pollution of the surrounding land. Meanwhile, trust in management must be built within the framework of trade in the Industrial Era 4.0, which is developing continuously in world trade relations. This study aimed to obtain information on the distribution of Cd in agricultural soils in the middle of the Serayu watershed in March-August 2017. A total of 220 soil samples were taken using the GRID method, and the analysis of Cd concentration was determined by atomic absorption spectrofotometry (AAS). The results showed that Cd was detected in 142 soil samples in the range of 1.0-<1.5 mg kg\(^{-1}\) and detected in the range of 0.5-<1.0 mg kg\(^{-1}\) in 78 soil samples. The results were non-normally distributed with a clustered distribution pattern. The average value of the distribution of Cd in agricultural land in the middle of Serayu watershed was 1.21 mg kg\(^{-1}\), and the highest Cd concentration was 2.18 mg kg\(^{-1}\). The Cd concentration in the middle of the Serayu watershed is classified within the safe category because the concentration is still below the critical Cd threshold value of 3-8 mg kg\(^{-1}\).

Keywords: agricultural land, cadmium, distribution, the middle of Serayu watershed

1. Introduction
Cadmium (Cd) is categorized as one of the non-essential heavy metals [1, 2], therefore at certain levels it can be toxic to organisms such as plants, animals and humans [3, 4]. Cd is not easily degraded in the environment [1, 5] but is easily absorbed by living tissue and remains in living tissue for a certain duration of time [4, 6]. The accumulation of Cd in agricultural products will enter the human body through the food chain. In the human body, Cd can trigger cancer, damage to the heart, liver, kidneys, lungs, and mutagenesis that can cause death [7, 8, 9, 10].
In agricultural land, Cd comes from various sources, including the weathering of the parent soil \[11\] and also from the use of agrochemicals. Chemical fertilizers containing phosphates can increase the concentration of Cd in the soil \[12, 13, 14, 15\]. Organic fertilizers such as manure also play a role as a source of Cd in agricultural land \[16–18\]. Some pesticides contain Cd, so they can also increase Cd contamination in the soil \[14, 19\]. The critical threshold for Cd contamination in soil is 3-8 mg kg\(^{-1}\) \[20\] and 0.2 mg kg\(^{-1}\) in agricultural products \[21\].

Serayu watershed is one of the watersheds that has severe land degradation \[22, 23\], where in the upstream part it is used for vegetable cultivation with the use of massive and high organic fertilizers. As an illustration, the use of organic fertilizers in potato cultivation in the upstream of Serayu watershed requires a manure of 10 t ha\(^{-1}\) each season \[24\]. The Middle of the Serayu watershed has a dual function, first as a recipient of the impacts of agricultural activities in the upstream watershed and secondly as a source of pollution for agricultural land in the downstream of Serayu watershed. Agricultural practices that ignored the principles of land conservation in the upstream area of the Serayu watershed have caused erosion rates to exceed the threshold \[22\] and this has increased steadily from year to year \[25\].

On the other hand, digitization has developed tremendously as a marker of the industrial era 4.0. People can do anything, anywhere and anytime by using digitization. People don’t have to meet in one place and time to make transactions. In this era, the only approach that can be taken is to build trust through good agriculture practices (GAP). One of the supporting elements of GAP is land which is chemically and biologically not degraded. This study is to determine the distribution of Cd on agricultural land in the middle of Serayu watersheds in order to support trade in the industrial era 4.0.

### 2. Materials and Methods

The research was conducted on March - August 2017 in agricultural land around the Middle of Serayu watershed using a survey method. Determination of soil sampling points is carried out in a grid method in units on the digital map of Rupa Bumi Indonesia. Boundary map units delineated in the field with the help of the ArcGIS program, based on the slope of the land. On flat land (slope \(<3\%) one sampling point can represented an area of 50-100 hectares, and on land with a slope of \(>3\%) one sampling point represented an area of 50 hectares \[26\]. Soil sampling carried out by Grid method, a composite soil sample consists of 5-7 subsamples, taken from topsoil (about 0-20 cm
depth. Analysis of Cd concentration was carried out in Terpadu Laboratory, IAERI in Pati, Central Java.

Soil samples were finely ground into powder after drying in room temperature. The Cd concentration in the soil was measured according to Manimaran et al. [27], with minor modification. Dried soil samples (1000 mg) were placed in digestion tubes containing 5 ml of a nitric acid and perchloric acid (5:1, v/v) mixture; the tubes were incubated overnight. The next day, the tubes were subjected to 8 h of digestion at 175 °C with gradual increases in the heat until 300 °C was reached, to allow the mixture to clear. The digested liquid was cooled overnight, followed by filtering through Whatman No. 1 filter paper. Then the volume was brought to 50 ml with deionized water. Cadmium concentrations in each sample were analyzed using an atomic absorption spectrophotometer (AAS, Varian-240 FS) and estimated using Cd solution standard curves, by formula below:

$$Cd \ (mg \ km^{-1}) = \frac{Ppm \ curva \times \frac{V}{1000 \ ml} \times \frac{1000 \ g}{W} \times fp \times fk}{1000 \ ml}$$

(1)

Notes:
- Ppm curva: the value of the Cd concentration obtained from the AAS reading, were estimated using Cadmium standard curves.
- V: extract volume (ml)
- W: weight of soil sample (g)
- Fp: dilution factor
- Fk: correction factor of water content

Descriptive statistical analysis was conducted to determine the distribution pattern of Cd concentration in soil, while to determine the correlation between Cd concentration and soil CEC were analyzed using the Pearson correlation.

3. Results and Discussions

3.1. Concentration of Cadmium in soil

Cadmium (Cd) can detected in all over of soil samples from agricultural land around the middle of Serayu watershed with a concentration range of 0.053-2.180 mg kg\(^{-1}\). The average of Cd concentration in the soil on agricultural land in the middle of Serayu watershed is 1.21 mg kg\(^{-1}\) (Figure 1a). The number of soil samples based on classification of the range of Cd concentration, there were 12 samples of Cd concentration <0.5 mg
78 samples of Cd concentration 0.5-<1.0 mg kg\(^{-1}\), 142 samples of Cd concentration 1.0-<1.5 mg kg\(^{-1}\), and 75 samples of Cd concentration >1.5 mg kg\(^{-1}\) (Figure 1b).

Figure 1: The distribution of Cd concentration in soil in the middle of Serayu watershed (a) and the number of soil samples based on the range of Cd concentration (b).

The characteristics of the soil in the research location have a parent rock in the form of clay deposits, calcareous and sandstone, andesite and basalt. These parent rocks become a source of Cd in the soil [30]. The application of fertilizer is thought to increase the Cd content in the soil. Synthetic or natural phosphate fertilizers, and nitrogen fertilizers containing Cd. Furthermore, the use of organic fertilizers in vegetable cultivation in the upstream Serayu watershed also contributed to the content of Cd in the soil.

3.2. Distribution of Cadmium

Descriptive analysis shows that the distribution of Cd in the soil was un-normally, that known from the value of skewness that close to -1 and have a clustered distribution pattern, that seen from the value of kurtosis approach to 0 (Table 1). The minimum Cd concentration was 0.053 mg kg\(^{-1}\) and the highest concentration was 2.18 mg kg\(^{-1}\), detected in agricultural land in Lawen Village, Kalibenning District, Banjarnegara Regency. However, the concentration of Cd in the soil around the middle of Serayu watershed was still below the critical level of Cd for soil of 3-8 mg kg\(^{-1}\) [20]. This showed that the level of Cd contamination in agricultural land around the middle of Serayu watershed is in the safe category for agricultural land. High concentration of heavy metals in the soil cause contamination in the soil [28, 29].

The presence of Cd in the soil affected the uptake of nutrients from the soil by plants [31, 32]. Application of N and K fertilizers also increased the solubility of Cd in the
TABLE 1: Descriptive statistical analysis of Cd concentration in the soil of the middle of Serayu watershed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of soil sampling</td>
<td>307</td>
</tr>
<tr>
<td>Cd detected in the soil samples</td>
<td>307</td>
</tr>
<tr>
<td>The average of Cd concentration (mg kg(^{-1}))</td>
<td>1.21</td>
</tr>
<tr>
<td>Minimum Cd concentration (mg kg(^{-1}))</td>
<td>0.053</td>
</tr>
<tr>
<td>Maximum Cd concentration (mg kg(^{-1}))</td>
<td>2.18</td>
</tr>
<tr>
<td>Deviation</td>
<td>0.404</td>
</tr>
<tr>
<td>CV (%)</td>
<td>33.33</td>
</tr>
<tr>
<td>Skewness</td>
<td>-0.256</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>-0.355</td>
</tr>
<tr>
<td>Critical limit concentration (mg kg(^{-1})) [20]</td>
<td>3-8</td>
</tr>
</tbody>
</table>

soil [33]. The characteristic of dissolved Cd in the soil is unstable, which facilitates the transformation of Cd from soil to plant parts, and accumulates in plant tissue [34, 35]. This is the concern of the community as consumer in receiving food products that are safely from Cd contamination.

3.3. The Relationship of Cadmium with Soil Chemical Properties

To determine the relationship between heavy metal concentrations and soil chemical properties, a simple correlation regression analysis was carried out (Figure 2), that showed the regression equation \( Y = 4.034x + 18.46 \). The relationship of Cd in the soil and the Cation Exchange Capacity (CEC) showed a positive correlation although it is a weak \((R^2 = 0.059)\).

Soil reactions are an important controlling factor for the chemical behavior of metals and various other important processes in the soil [36, 37]. Soil negative charge is an important factor of colloidal clay and soil organic matter. The clay content of the soil has a high affinity for heavy metals, thus reducing the availability of heavy metals [38]. The increase in the negative charge of the clay can increase the cation absorption capacity in the soil. Furthermore, there will be a process of deposition of metal ions in the soil solution into unavailable forms and will reduce the effect of heavy metals absorbed by plants [39, 40]. The mobility and availability of heavy metals depends on the method and strength of heavy metal fixation by soil components, especially by clay fractions [39–41].

The high concentration of C-organic in the soil increases the concentration of organic matter in the form of humic acid and fulvic acid [42]. Humic acid and fulvic acid are parts that have a major role in the chemical reactions of organic materials, where humic acid
has functional groups such as –COOH, -OH phenolics and –OH alcoholates. Thus humic acid has the opportunity to form complexes with metal ions [43, 44]. Organic matter in the soil has an effect on CEC [16, 45] and absorbs heavy metals in complex forms [16, 46].

4. Conclusions

All soils from the observation point were detected Cadmium with concentration between 0.053-2.18 mg kg\(^{-1}\). The Cd concentration in agricultural land around the middle of Serayu watershed was distributed un-normally with a clustered pattern. The Cd concentration is still below of the soil Cd quality standard, which is less than 3-8 mg kg\(^{-1}\), then it is safe from cadmium contamination to support trade in the agricultural sector in the industrial era 4.0.

Acknowledgments

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Principles of soil chemistry review


