

Original Research

Assessment of Soil Contamination by Heavy Metals: A Case of Vegetable Production Center in Banjarbaru Region, Indonesia

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Received: 5 March 2022

Accepted: 29 August 2022

Abstract

Landasan Ulin is a center for vegetable production, and it has an important role in producing vegetables for the city of Banjarbaru. Agricultural soil in this study was assessed for heavy metal contamination using the geoaccumulation index (I_{geo}), contamination factor (C_f), the degree of contamination (C_d), the degree of modified contamination (mC_d), and the Pollution Load Index (PLI) as well as magnetic susceptibility. Samples were collected from topsoil and analyzed using magnetic susceptibility and Atomic Absorption Spectrophotometer (AAS). The average concentration of heavy metals in the sampling area A is Fe>Zn>Mn>Cu>Hg, and the area B is Fe>Mn>Zn>Cu>Hg. Magnetic susceptibility values in area A is higher than in area B and the value of magnetic susceptibility can be used as a proxy for monitoring heavy metal concentrations, especially Zn in this area. Zn and Cu exceeded the threshold set by the Indonesian Standards Institute. Igeo results show that the research area is moderately contaminated with Cu, Zn, and Hg. According to C_f , the soil was classified as low contaminated with Fe, Zn, Cu, Mn, and Hg, as well as Cd and mCd. The PLI results show that in both area, drastic corrective action is not required.

Keywords: geoaccumulation index, contamination factor, contamination degree, pollution load index

Introduction

Heavy metal contamination of agricultural soil due to chemical fertilizers and pesticides is a serious ecological problem today [1, 2]. In agricultural soil, the

continuous use of manure and chemical fertilizers for a long time will result in higher heavy metal content [3, 4]. Some heavy metals are needed for the growth of certain plants [5], but some of them for humans can be toxic. When these heavy metals are absorbed and accumulated by plants and then consumed by humans, this will pose a risk to the human body [6].

Some heavy metals have been found in agricultural land in several areas in Indonesia, such as Pb found

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in soil from 168 locations with different land use and traffic conditions in Yogyakarta, Indonesia [7]. In Semarang, Indonesia, the paddy field contains heavy metals Pb, Cd, and Cu [8]. In agricultural land in Karawang, Pb and Cd were found with concentrations exceeding 1.0 ppm [9]. Meanwhile, in agricultural soils in Bangladesh for the dry season, heavy metals were found with concentrations of $As > Fe > Hg > Mn > Zn > Cu > Cr > Ni > Pb > Cd$ and in the rainy season $As > Fe > Mn > Zn > Hg > Cu > Ni > Cr > Pb > Cd$ [10]. In paddy soils at Hunan Province, China, there was founded heavy metals (Cd, Cr, As, Ni, Mn, Pb, and Hg) in three different locations [11].

The presence of magnetic minerals in the soil can come from weathering of the parent rock (lithogenic origin) and can also come from human activities (anthropogenic). Magnetic minerals that are commonly found in soil are hematite and magnetite. Their presence is in the form of solid waste which can act as the main absorber of pollutants such as heavy metals in the soil. Their presence in the soil will affect the value of the magnetic susceptibility of the soil. The use of magnetic susceptibility has been widely used in various soil science studies, such as soil morphology and genesis as well as tools for mapping the distribution of environmental pollutants [12]. Magnetic susceptibility measurement has been considered as a fast and cheapest monitoring tool for determining the spatial distribution of heavy metal presence in soil and can be used as a proxy for chemical methods [13]. Research using the method of environmental magnetism in Indonesia is still few in number. Several studies were conducted to examine the river and lake environment [14-17]. Therefore, this study is very important.

Landasan Ulin is a vegetable center production in Banjarbaru City, South Kalimantan, Indonesia. Agricultural activities in this area are carried out by farmers traditionally [18]. Meanwhile, agricultural land has the potential to experience heavy metal pollution, and studies on heavy metal pollution in agriculture in this area are still rarely carried out. Therefore, it is very important to conduct this research to determine the current status of the presence of these heavy metals on the surface of agricultural soil. This will be of benefit to ameliorate the impacted environmental problems further, and to adopt mitigation strategies in the future. This study aims to investigate the level of contamination of various heavy metals (Fe, Mn, Cu, Zn, Hg) in agricultural land located in Landasan Ulin, South Kalimantan, Indonesia, using different indices such as geoaccumulation index, pollution factor, degree of pollution, and the pollution load index. The correlation between heavy metal contamination and magnetic susceptibility is also investigated in this study. These results can be used as an alternative method in determining heavy metal contamination in agricultural areas. This approach will help monitor the presence of heavy metals in agricultural soils and soil remediation. Monitoring for polluted areas is crucial, and it is

beneficial for the sustainability of pollution management and control in the future.

Materials and Methods

Study Area

Sampling and Measurements

Index of Geoaccumulation, Contamination Factor (C_f), Degree of Contamination (Cd) and Pollution Load Index (PLI)

Landasan Ulin, South Kalimantan Province, Indonesia, has a 92.42 km² area, consisting of mountains and hills in the north and east, and lowlands to the west, while the south has alluvium and swamp areas. Landasan Ulin is about 40 km from the provincial capital, Banjarmasin. Landasan Ulin is a vegetable production area in South Kalimantan. The cultivated vegetables from the area include mustard greens, kale, spinach, eggplant, lettuce, long beans, peanuts, and scallions. One of the efforts to increase the yield and quality of vegetables is through fertilization. Both organic and inorganic fertilizers are applied. The used dose of organic fertilizer was 485 kg, or an average of 16.17 kg/farmer, while the inorganic fertilizer was 556 kg, or an average of 18.53 kg/farmer. Nitrogen (N) fertilizer is critical for the growth of vegetables. The crops are never separated from the disturbance of weeds and pests. Theoretically, weeds are bothering vegetable growth because they are competitive in many ways, especially in getting water, sunlight, and nutrients. Weeds also, in some cases, become the source of the disease that often becomes a significant threat to the crops. To manage the growth of weeds, farmers do the chemical control of weeds regularly by using Gramoxon. About 400 liters is enough to kill weeds on an average of 13.33 liters/respondent. Removing the weeds can also be done manually by using physical measures or machinery. Meanwhile, in overcoming pests and diseases in North Landasan Ulin Village, the farmers used Ampligo, one of the pesticide brands. It is sprayed regularly with a dose that ranges from 20 liters or an average of 0.67 liters/farmer to kill/destroy pests that stick around the leaves and stems of mustard greens [19].

Twelve agriculture soil samples were taken from two different area (Site A and site B) (Fig. 1). In general, agricultural soils in these two areas tend to be homogeneous, with the chemical composition of the soil having low variability [19]. But geologically, these two areas are in two different formations. Site A is in the Dahor Formation and Site B is in alluvial soil [20]. That is why this research is divided into two different research areas. These samples were collected using the sampling procedure based on Rahman's methods. Approximately 250-300 g of agricultural soil

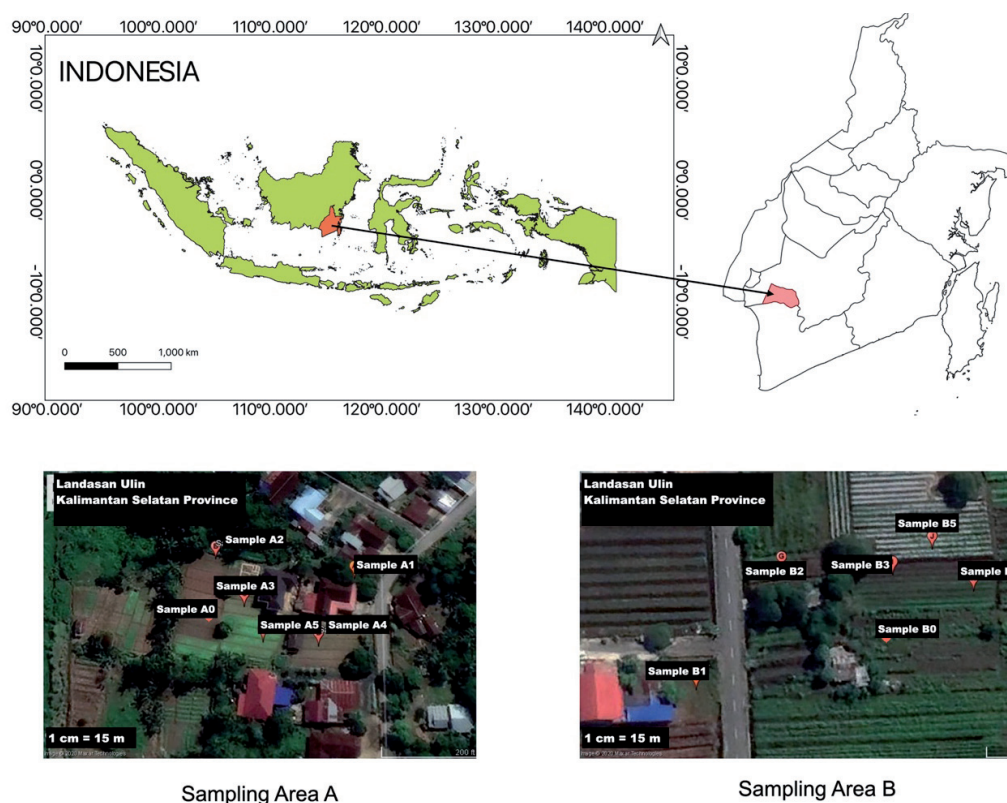


Fig. 1. The sampling site of agriculture soil from vegetable production center in Banjarbaru Region.

were collected from the soil surface layer (15-20 cm) using a stainless steel grab sampler. The difference in distance from one sampling point to another in one location is about 100 m. The sample taken is in the center to avoid contact with the inside of the grab sampler material. Samples are checked for possible contamination. Then the sample was transferred to a previously cleaned plastic container [21]. In the laboratory, the soil sample was dried by aerating at room temperature. The dry soil samples were sieved using a 325 mesh-size sieve (44 μm in diameter) to obtain homogeneous soil particles. 2-3 g dry soil samples were digested in about 15 mL of aqua-regia ($\text{HCl}:\text{HNO}_3 = 3:1$) for about 4-5 hours on a hotplate set to 110°C. The materials were then diluted to 50 mL in a 100 mL Pyrex glass beaker with distilled water. In the laboratory of the Indonesian Geological Survey in Bandung, Indonesia, by AA280FS Atomic Absorption Spectrometer (AAS) (Variant Inc. Palo Alto, USA), the solution was filtered, and the filtrates were examined. The working standard solutions for each metal were prepared before every analysis. An air acetylene flame AAS was used to measure Fe, Zn, Cu, Pb, and Mn concentrations, with As determined by hydride vapor generation AAS. Magnetic susceptibility measurement was carried out in the following way, the dried soil sample was put into a cylindrical plastic holder with a diameter of 25.4 mm and a height of 22 then measured using a Susceptibilitymeter (Bartington Instrument Ltd., Oxford, UK). Each sample was measured with

three repetitions. The magnetic susceptibility value used is the average value of the results of this measurement [13].

To analyze the level of heavy metal pollution in an area, more than one pollution index analysis is needed (3, 21, 36, 37), so in this study 5 pollution indices were used, namely the geoaccumulation index (I_{geo}), contamination factor (C_f), the degree of contamination (Cd), the degree of modified contamination (mCd), and the Pollution Load Index (PLI). The five pollution indices are expected to provide more accurate information on the level of pollution in this research area.

Müller's geoaccumulation index (I_{geo}) [22], which was originally established to measure contamination of sedimentary bottoms, may now be used to assess soil contamination. It's calculated using Equation (1) as follows:

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5B_n} \quad (1)$$

C_n is the element's observed concentration in the pelitic sedimentary fraction (<2 m), and B_n is the geochemical background value based on argillaceous sedimentary fossils (shale mean). C_f and C_d are indices that can be used to assess soil contamination which consists of four classes [23]. Equation (2) was utilized in the following way:

$$C_f^i = \frac{C_0^i}{C_n^i} \quad (2)$$

C_0^i is the pre-industrial concentration of the specific metal, and C_n^i is the mean content of metals from at least five sampling sites. As a result, the computed C_d is defined as the amount of C_f^i determined by Hakanson for the polluting species [23]. The following is the equation used to calculate C_d

$$C_d = \sum_{i=1}^n C_f^i \quad (3)$$

C_d is intended to measure the overall level of contamination in the surface layer at a particular sampling site. In this study, we applied a factor modification as applied by Krzysztof [24]. Abraham [25] proposes the following modified and generalized version of the Hakanson equation [23] for estimating the total degree of contamination at a sample or coring location. Equation (4) is a modified equation for the general approach to calculating contamination levels.

$$mC_d = \frac{\sum_{i=1}^n C_f^i}{n} \quad (4)$$

Where n denotes the number of elements to be examined and the contamination factor is abbreviated as C_f^i . Using this formula to compute mC_d allows metals to be incorporated into studies with no upper limit. To identify pollution, Tomlinson created the pollutant load index (PLI) [26]. This index allows for comparisons of pollution levels between sites and across time. The PLI was calculated as a concentration factor for each heavy metal in relation to the soil background value. The background for the heavy metal in this investigation was the average world concentration of the examined metal reported for shale [27]. PLI can assess the level of metal contamination and the actions that must be taken. The formulas used are in the form of Equation (5).

$$PLI = n\sqrt{C_{f1} \times C_{f2} \times \dots \times C_{fn}} \quad (5)$$

Results and Discussion

Heavy Metal Content and Magnetic Susceptibility

Soil Pollution Degree

Correlation Between Heavy Metal Content and Magnetic Susceptibility

Table 1 shows the average concentrations of a number of metals in the agricultural soils of the study area. The average Fe, Zn, Mn, Cu, and Hg

concentrations in study area A were 28,850.00, 91.67, 89.33, 86.00, and 0.10 mg/kg. The average amounts of Fe, Zn, Mn, Cu, and Hg in B were 3,166.00, 25.67, 33.00, 7.50, and 0.01 mg/kg, respectively. Metal trends in research area A are Fe>Zn>Mn>Cu>Hg. Meanwhile, the trends of metals according to the average concentration in study area B is: Fe>Mn>Zn>Cu>Hg. Due to the agronomic practice, the concentration of heavy metals in study area B was various. Meanwhile, metal concentration trends in study area B are as follows: Fe>Mn>Zn>Cu>Hg. The concentration of heavy metals in study area B varied due to agronomic practices. The low heavy metal concentration in the soil can be attributed to the constant elimination of heavy metals by vegetables grown in the designated regions [21]. Table 1 also includes the magnetic susceptibility values of the samples from areas A and B. In general, the magnetic susceptibility values of area A ($100.0 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$) were 9 times greater than those of area B ($12.2 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$). Magnetic susceptibility of sampling area A ranges from 44.8 to $136.5 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$, while magnetic susceptibility of sampling area B ranges from 1.1 to $24.3 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$. Agricultural practices, such as the use of magnetic minerals such as Fe in fertilizers and pesticides, can increase the magnetic mineral content of agricultural soil. Magnetic minerals in agricultural soil can also be found in household waste. As is well known, the research site, area A, is located very close to settlements, whereas area B is located far from settlements. Household waste contains anthropogenic magnetic minerals, which can raise the magnetic susceptibility value [28].

The content of Mn and Cu at point A1 in area A is higher than at other points, which are suspected to be from fertilizers and pesticides [36], as well as traffic waste [28, 29] and Zn. This is known because of the proximity of point A1 to the highway. Furthermore, the high Mn content at point A1 is thought to be the result of post-harvest processing of agricultural land [38].

The average I_{geo} and contamination levels of several metals in soil are shown in Table 2. I_{geo} is highly variable, implying that the soil surrounding the sampling area was uncontaminated to moderately contaminated in terms of the metals tested. The average concentration of heavy metals was higher in study area A than in site B. Long-term use of machine tools, paints, pigments, and industrial equipment in the study area may have caused the highest Fe content in the soil [10]. The average concentration of Zn, Mn, Cu, and Hg found in study area A was also higher than in study area B. The presence of heavy metals in this area was suspected due to agricultural practices. Pesticides contain the elements Mn, Zn, and Cu (Cu, As, Hg, Pb, Mn, and Zn). Fungicides contain the elements Cu, Zn, and Mn. Compost and manure also contain Zn and Cu. Seed dressings contain Hg [30-32].

Zn is present in all sampling points at study area A, but not all sampling points at location B. Zn concentrations were approximately three times higher

Table 1. Different heavy metal concentrations and magnetic susceptibility in the study area's agricultural soil.

Sample	Fe	Zn	Mn	Cu	Hg	$\chi_{\text{rf}} (\times 10^{-8} \text{ m}^3 \text{ kg}^{-1})$
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
Sampling Area A						
A0	28,600.00	156.00	112.00	49.00	0.12	136.50
A1	28,100.00	124.00	161.00	147.00	0.12	135.60
A2	27,300.00	77.00	60.00	70.00	0.08	100.10
A3	26,900.00	57.00	52.00	70.00	0.11	135.60
A4	31,800.00	65.00	70.00	89.00	0.09	47.30
A5	30,400.00	71.00	81.00	91.00	0.11	44.80
Min	26,900.00	57.00	52.00	49.00	0.08	44.80
Max	31,800.00	156.00	161.00	147.00	0.12	136.50
Mean	28,850.00	91.67	89.33	86.00	0.10	100.00
SD	1,893.94	39.00	41.00	34.00	0.01	44.03
Sampling Area B						
B0	2,500.00	20.00	38.00	7.00	0.01	23.30
B1	1,500.00	21.00	23.00	7.00	0.04	21.00
B2	1,000.00	65.00	15.00	5.00	0.01	24.30
B3	8,200.00	14.00	68.00	12.00	0.01	1.10
B4	4,800.00	14.00	39.00	9.00	0.01	1.90
B5	1,000.00	20.00	15.00	5.00	0.01	1.60
Min	1,000.00	14.00	15.00	5.00	0.01	1.10
Max	8,200.00	65.00	68.00	12.00	0.04	24.30
Mean	3,166.67	25.67	33.00	7.50	0.01	12.20
SD	2,850.03	19.52	20.17	2.66	0.01	11.74
Baseline	4.72	95.00	850.00	45.00	0.40	-

in sampling points at site A than in sampling points at site B. The average Zn concentration at sites A and B exceeded the 0.06 mg/kg threshold set by the Indonesian National Standardization Agency. However, the Zn concentration at these two sites was still low when compared to agricultural soils in Shenzhen, China (concentration average of 194 mg/kg in the dry season and 209 mg/kg in the rainy season) [33], soil in an unpolluted area of Gebze, China (concentration average 632 mg/kg) [34], and agricultural soil from Huanghuai Plain, China (74 mg/kg) [35]. In contrast to Zn, Cu was distributed over all sampling points in both study locations, and the concentration in site A was ten times higher than in site B.

The average Cu concentration in both locations also exceeded the 0.04 mg/kg threshold set by the Indonesian National Standardization Agency. However, the concentration of Cu at these two locations was still low when compared to agricultural soils in Shenzhen, China (with an average of 60 mg/kg in the rainy season

and 90 mg/kg in the dry season) [33], as well as soils in unpolluted areas in Gebze, China (concentration average 95.88 mg/kg) [34], palm farms' soil in Morocco (concentration average 138 mg/kg) [36], and agricultural soil from Patuakhali District, Bangladesh (4.1-181 mg/kg) [37]. However, the Cu content at Site A was higher than the Cu content in agricultural soils in the Dumuria Upazila, Bangladesh [38] and Marrakech, Morocco [39] areas, whereas the Cu content at Site B was lower than the Cu content in agricultural soils in the Dumuria Upazila, Bangladesh (concentration average 17.70 mg/kg) and Marrakech, Morocco. Cu concentrations are higher in these two locations than in agricultural soils from Jeddah, Arab Saudi Arabia (concentration average 0.4 mg/kg) [40].

Hg concentrations were four times higher in site A than in site B. The presence of Hg was suspected to be the result of fungicide use. Hg in soil can be produced by a number of activities, including basic metal processing, some chemical sector activities, mining, and industrial

Table 2. Average I_{geo} and contamination levels of the soil in two sampling areas.

Element	Sampling Area A		Sampling Area B	
	I _{geo} Value	Contamination Level	I _{geo} Value	Contamination Level
Fe	-1.3	Unpolluted	-4.94	Unpolluted
Zn	-0.74	Unpolluted	-2.71	Unpolluted
Mn	-3.95	Unpolluted	-5.49	Unpolluted
Cu	0.27	Moderately to strongly polluted	-3.24	Unpolluted
Hg	-2.53	Unpolluted	-5.57	Unpolluted

Table 3. Average C_fⁱ, C_dⁱ, mC_dⁱ, and PLI of soil over two sampling areas.

	Sampling area A	Sampling area B
C _f Fe	0.61	0.07
C _f Zn	0.96	0.27
C _f Mn	0.11	0.04
C _f Cu	0.95	0.17
C _f Hg	0.26	0.04
Cd	2.89	0.58
mCd	0.48	0.1
PLI	0.42	0.07

waste. Hg concentrations in Gebze soil ranged from 9 to 2.721 g/kg, with an average of 102 g/kg [34], which is significantly higher than the concentrations found

in this study. The Hg content of agricultural soils in China's Gorges Dam area is similar to that of this study area (0.08 mg/kg) [41]. Hg levels in sites A and B did not exceed the 0.5 mg/kg threshold for its presence in soil. According to this research, the concentration of heavy metals in site A is higher than in site B. According to observations and interviews with local farmers, site A was used for plantation activities much earlier than site B. Heavy metals accumulate in the soil over time due to a variety of factors, including the use of fertilizers, pesticides, and agricultural equipment [42, 43].

C_f was used to determine the overall contamination of the analyzed agricultural soil. The soil was classified as having a low contamination factor in both test regions, indicating low contamination with Fe, Zn, Mn, Cu, and Hg. The maximum contamination degree (C_d) values indicated a low level of contamination. As proposed in this work, the mC_d is calculated by combining and averaging all available analytical data for a collection of soil samples.

Table 4. Pearson correlation (R) between heavy metal contents and magnetic susceptibility. The value of R for strong (above 0.5) correlation is in bold.

	Fe	Zn	Mn	Cu	Hg	χ _{if}
Sampling area A						
Fe	1					
Zn	-0.163	1				
Mn	-0.029	0.77	1			
Cu	0.114	0.03	0.656	1		
Hg	-0.145	0.6	0.658	0.239	1	
χ _{if}	-0.831	0.555	0.392	-0.025	0.49	1
Sampling area B						
Fe	1					
Zn	-0.5	1				
Mn	0.965	-0.541	1			
Cu	0.977	-0.573	0.964	1		
Hg	-0.286	-0.117	-0.243	-0.092	1	
χ _{if}	-0.586	0.595	-0.431	-0.506	0.367	1

As a result, this improved method may provide a thorough assessment of the overall enrichment and contamination impact of various pollutant groups in the soil. In both sampling areas, the mC_d ranged from 0.48 to 0.10, indicating nil to a very low level of contamination. The PLI values indicated that drastic rectification measures are not needed in both areas. Table 3 shows the soil's average C_f^i , C_d , mC_d and PLI.

Pearson correlation analysis [44] was used to compare all of the variables. Table 4 displays the correlation coefficients between metal pairs. High correlation values ($R > 0.50$) between different metal pairs, indicating soil accumulation. In soil samples from sampling area A, Mn-Zn ($R = 0.770$), Cu-Mn ($R = 0.656$), Hg-Zn ($R = 0.600$), and Hg-Mn ($R = 0.600$) had high correlation values ($R > 0.5$). The correlation trends in sampling area B were: Fe-Mn ($R = 0.965$), Fe-Cu ($R = 0.977$), and Cu-Mn ($R = 0.964$).

Significant correlations indicate that they are thought to be anthropogenic, originating in agricultural activities such as the use of fertilizers and pesticides. Both of these areas are about 2 kilometers from Syamsuddin Noer airport, which is thought to contribute to heavy metal accumulation in the soil in this area [45]. Table 4 also shows the correlation coefficient between each heavy metal content and magnetic susceptibility measured in the same soil plane. According to the correlation analysis of each plot of land, several heavy metals show a positive correlation with magnetic susceptibility values, namely Zn ($R = 0.555$), Mn ($R = 0.392$), and Hg ($R = 0.490$) in area A, and Zn ($R = 0.595$) and Hg ($R = 0.367$) in area B. When compared to other heavy metals, the content of the heavy metal Zn in both soil planes showed a stronger positive correlation coefficient with magnetic susceptibility. In both sampling areas, heavy metals such as Fe and Cu have negative correlation coefficient values with magnetic susceptibility.

Conclusions

In the biosphere, the soil is an essential component, every harmful change of it can seriously affect the quality of human life. It is very possible to have heavy metals content in the soil. Heavy metals that enter the food chain are the most detrimental because they can threaten human health. Some of the agricultural lands in Landasan Ulin, Banjarbaru, South Kalimantan are observed in this study. The lands were evaluated for the impact of anthropogenic heavy metals by using several indices that showed that study area A was not contaminated until moderately contaminated by different metals. Meanwhile, study area B did not show any contamination based on all indices. However, the presence of Cu and Zn in this region has exceeded the threshold set by the Indonesian National Standardization Agency, and this must be watched out for. For this reason, regular monitoring of heavy metals in

agricultural land is necessary to ensure environmental quality. In addition, remediation measures need to be carried out on agricultural land indicated to be contaminated by Cu and Zn. This study also shows that magnetic susceptibility can be used as a proxy for monitoring the concentration of heavy metal especially Zn in agricultural soil in the Landasan Ulin area.

Acknowledgments

This study was funded by DIPA Lambung Mangkurat University 2021.

Conflict of Interest

The authors declare no conflict of interest.

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