International Journal of Hydrological and Environmental for Sustainability
Volume 2, Issue 3, 104-112.
e_ISSN: 2828-5050
https://www.journal.foundae.com/index.php/ijhes

X-Ray Fluorescence Monitoring Metal Content and Nutrient Elements for Predicting Soil Fertility Parameters Based on pH in Ultisol Soil

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Article Info

Article history:

Received: September 19, 2023
Revised: October 20, 2023
Accepted: October 29 2023

Abstract

Soil fertility parameters, including macronutrients, micronutrients, and metal content, are very important for optimizing agricultural and plantation land management. Ultisol is a type of soil that is commonly used as a planting medium for oil palm plantations, rubber, and various types of vegetables. Continuous land use causes variations in nutrient and metal content. This change is also caused by the fertilization process and the characteristics of the plants grown in the area. In this study, an analysis of soil fertility parameters (macronutrients, micronutrients, and metal content) was analyzed using X-Ray Fluorescence (XRF) on Ultisol soil taken from Muara Jambi Regency, Indonesia. This analysis was conducted across land-use areas (Palm, Rubber, Vegetables, and Forest). Subsequently, the obtained measurements were used to model correlations with soil pH values to predict soil fertility parameters. The quantitative results showed that the metal content values were reasonably consistent across all locations regarding metal types and their percentage concentrations. However, locations 1 (T1) and 2 (T2) have higher aluminum (Al) content than locations 3 and 4 and lower magnesium (Mg) content. The modeling, when correlated with pH values, indicated that metal elements correlated 0.938, macronutrients 0.934, and micronutrients 0.767. From these correlations, it can be qualitatively inferred that there is a strong relationship between pH and the presence of metal content, macronutrients, and micronutrients. In the future, this can serve as a model for estimating the presence of soil fertility parameters.

Keywords: macronutrients; micronutrients; metal content; pH; ultisol; x-ray fluorescence

To cite this article: Samsidar., Maison., Ermadani., Latief, M., Pebralia, J., Riany, H., Amanda, D, R. and Maulana, L, Z. (2023). X-Ray Fluorescence Monitoring Metal Content and Nutrient Elements for Predicting Soil Fertility Parameters Based on Ph in Ultisol Soil. *International Journal of Hydrological and Environmental for Sustainability, 2*(3), 104-112. https://doi.org/10.58524/ijhes.v2i3.290

INTRODUCTION

Soil nutrients are a crucial factor that determines soil fertility. Various analyses are required to ascertain the levels of these nutrients, including conventional laboratory measurement methods such as the soil extraction method. This method involves extracting soil components using specific chemical solutions to obtain the concentrations of dissolved nutrients. It can be used to measure mineral, organic, and non-organic materials (Pansu., 2003). Furthermore, characterization methods can be used to measure metal content and other nutrients, including X-Ray Fluorescence (XRF). This tool was used to detect the presence of elements such as P, Ca, Cu, and Zn (Janovsky et al., 2020). Portable X-Ray Fluorescence (p-XRF) has been developed for nutrient element testing (Xu et al., 2019; Lima et al., 2019; Andrade et al., 2020). This test covered soil nutrients (Ca, Mg, K, and P) and Al. Machine learning algorithms are then used to predict other nutrient contents (Benedet et al., 2021).

Changes in land use, along with the fertilization processes and types of plants present on the land, influence the presence of nutrients and other metals. Fertilization positively affects Nitrogen, Phosphorus, and Potassium concentration changes but does not influence the concentrations of Calcium and Magnesium (Hejman, et al., 2013). Fallow land, shrubland, and man-made grasslands can be recommended to enhance soil nutrient content (Ge, et al., 2020).

Information on nutrient elements and metal content is vital for evaluating frequent land-use changes. However, measuring these elements is not easy, as it requires time and often incurs high characterization costs. Thus, efforts are required to correlate them with specific parameters to simplify the estimation. One such potential correlation is with pH values. Several studies have suggested a relationship between the pH, nutrient elements, and metal content. One such correlation includes the effect of an increase in the soil pH. Such an increase can occur alongside fertilization, with a rise of up to 0.3 pH units over a decade (Minasny et al., 2016). An increase in pH is also accompanied by a reduction in Mn and Fe contents (Gryboys, M, et al., 2009; Bahera and Shukla., 2014).

Subsequent correlation reviews regarding nutrient and metal elements, biochemical processes, and microbes that affect the presence of nutrient elements were also undertaken. That included the correlation of pH with macronutrients (Ca, K, Mg, P, S), micronutrients (Cu, Fe, Mn, Se, Zn), and other elements (As, Cd, Pb). Based on the test results, pH strongly correlated with elements (Ca, Mg, P, and Mn) (Meille, et al., 2021). There is also a correlation between metal elements and pH (Sintorini et al., 2021). The influence of pH on the availability of nutrient elements and certain toxic elements has been described by Barrow., (2016). Changes in pH also affect microbial activity and the C and N cycle rates (Kemmit, et al., 2006). PH significantly influences soil biochemical processes (Neina, D., 2019) and mineralization (Curtin, et al., 1998). Therefore, pH is often referred to as the parent soil variable. It means that by knowing the pH value, other variables can be predicted. Therefore, soil pH can be widely applied to predict nutrient cycles and plant nutrition.

Numerous studies have examined how pH influences nutrients and other elements, but the magnitude of this effect has yet to be fully elucidated. Therefore, this research conducted a multiple linear regression model to determine the extent of the relationship between pH and metal elements, as well as macro and micronutrients. The application of this prediction model has been widely done. For example, a prediction model for soil nutrient elements produced a measurement accuracy of R=0.91 for organic soil materials and clay with R=0.93 (Helfer et al., 2020). The prediction of metal content with linear regression correlated with the metal content in plants is described by Ivezic, et al., (2015). Soil fertility predictions, after testing soil nutrient content (Ca, Mg, K, and P) and the Al element using portable X-Ray fluorescence (p-XRF), are outlined by Benedet et al., (2021). Therefore, understanding the correlation between pH and soil metal and nutrient elements is hoped to serve as an initial prediction model that can be further developed, especially for Ultisol or soils with pH<6.

METHOD

Soil Sampling

The soil samples used were from Ultisol soil found in the plantation area of Jambi Luar Kota in the Muara Jambi district. The sample collection areas consist of a palm plantation located at 1^{0} 37'25"S and 103⁰31’10”E (Location 1), a mixed plantation comprising palm, rubber, and forest located at 1⁰ 37’17”S and 103⁰ 31’10”E (Location 2), a natural forest area at 1⁰ 37’8”S and 103⁰ 31’6”E (Location 3), and a vegetable plantation situated at 1⁰37’8”S and 103⁰31’18”E (Location 4). Samples were taken from the surface (0-20cm) labeled T (Top) and deeper layers (20-50cm) labeled S (Sub) using a soil auger. The map of the sample collection area can be seen in **Figure 1**, and the specific sampling points are illustrated in **Figure 2**.

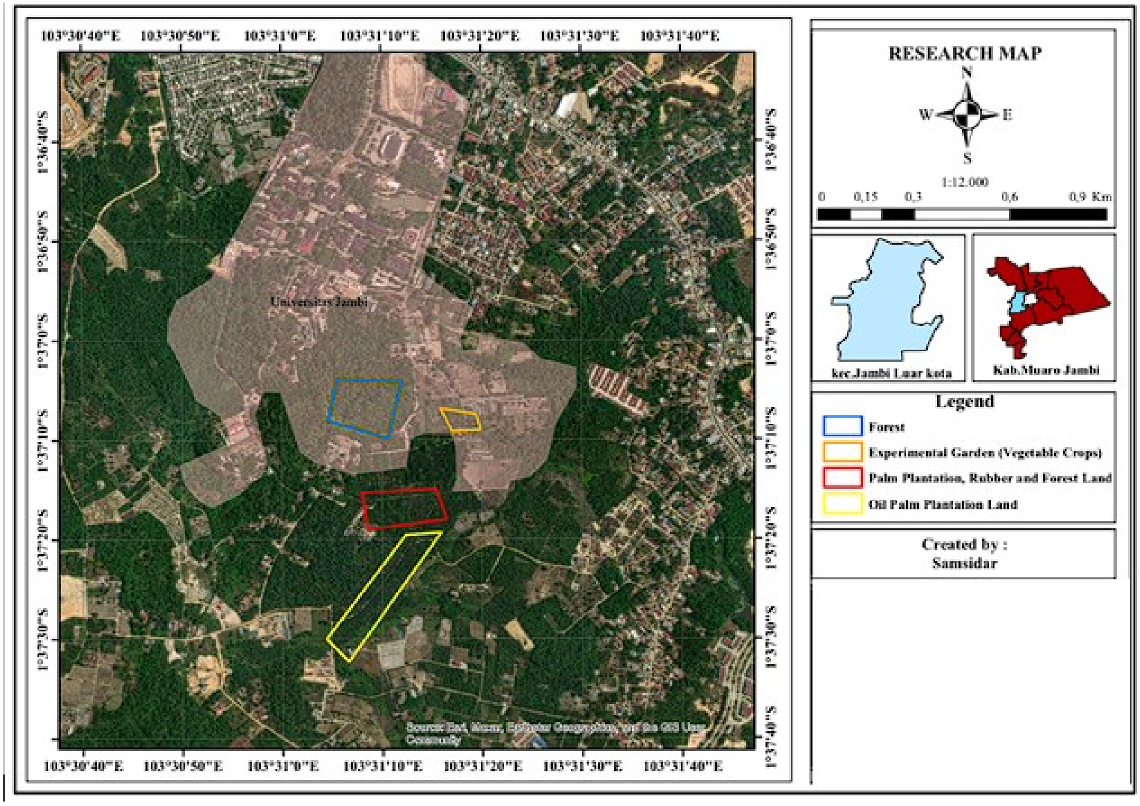

Figure 1. Research Location Map

Sampling was conducted by plotting a 10 m x 20 m area at each location **(Figure 2)**. Subsequently, at each location, five samples were taken from the Top layer (0-20cm) and five samples from the Sub layer (20-40cm), which were then mixed (Walworth., 2006).

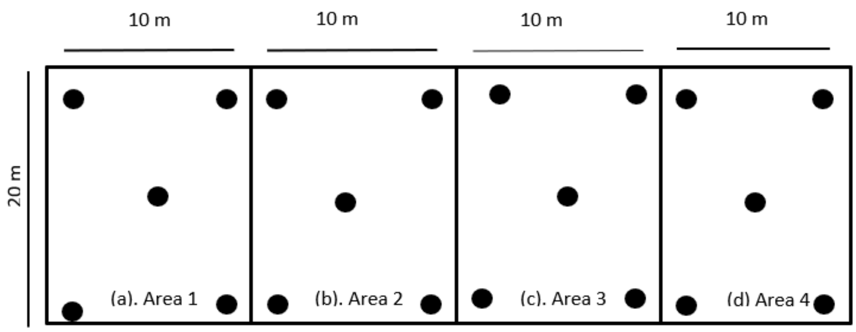

Figure 2. Plot of Sample Collection Points

Preparation and Analysis of Soil

Sample preparation began with air drying the samples. Subsequently, the samples were ground and sieved through a 15 mesh/< 2 mm sieve. For analysis using X-Ray Fluorescence (XRF), 10 grams of each sample was first weighed. The XRF instrument used was the S2 PUMA Series 2. The samples were placed in holders with diameters ranging from 40 mm to 152 mm. Measurements were then conducted to identify the metal content elements. For laboratory testing, measurements were taken for pH (H2O, 1:2), total nitrogen (Kjeldahl method), organic carbon (Walkley and Black method), and available phosphorus (Kurt Bray 1 method).

RESULTS AND DISCUSSION

From X-ray Fluorescence (XRF) measurements, metal elements, micronutrients, and several macronutrients such as K, Ca, Mg, and S were identified. Subsequent laboratory testing revealed values for total nitrogen (Kjeldahl method), which were then converted to percentages to standardize units for easier modeling, available phosphorus, organic carbon, and pH values. The distribution for each element and pH can be seen in **Table 1**.

Table 1. Distribution of metal content, nutrient elements, and pH across different locations.

	Element	Sample code							
		T1	S1	T2	S2	T3	S3	T4	S4
Metal Element (%)	Mg	4,30	5,72	4,35	4,35	4,08	5,65	**3,08**	3,46
	Al	**20,52**	21,82	16,08	20,30	19,23	20,59	**22,08**	23,34
	Si	59,62	54,45	67,22	62,16	61,15	58,05	57,21	54,73
	Fe	11,26	13,43	8,16	9,19	11,71	12,03	**12,25**	13,60
	S	0,08	0,05	0,09	0,08	0,11	0,07	0.08	0,05
	Cl	0,06	0,05	0,06	0,07	0,08	0,06	**0,03**	0,03
	K	0,58	0,61	0,46	0,43	0,43	0,42	0,61	0,41
	Ca	0,04	0	0,36	0,13	0,04	0	**1,35**	0,91
	Ti	3,09	3,37	2,75	2,84	2,72	2,67	0	2,98
	Zn	0,01	0,01	0,01	0,01	0,01	0,01	**0,02**	0,01
	Zr	0,31	0,32	0,28	0,29	0,31	0,30	**0,25**	0,29
	Ni	0	0	0,01	0,01	0,01	0,01	0,01	0,01
	Ga	0,01	0,01	0	0,01	0	0,01	0	0,01
	Mn	0,01	0,02	0,02	0,01	0,02	0,01	**0.05**	0,02
	Cr	0,04	0,04	0,05	0,05	0,03	0,03	0,05	0,03
	Rh	0	0	0,02	0	0	0	0,02	0
	Ta	0	0,02	0,02	0,02	0,02	0,02	0,02	0,02
	V	0,07	0,08	0,06	0,07	0,06	0,06	0,07	0,09
Macro Nutrients (%)	N	0,286	0,286	0,287	0,288	0,143	0,143	0,144	0,288
	P	0,0019	0,00048	0,016	0,0013	0,0010	0,00049	0,0043	0,0014
	C	0,041	0,035	0,060	0,040	0,065	0,050	0,048	0,033
	K	59,62	54,45	67,22	62,16	61,15	58,05	57,21	54,73
	Ca	0,04	0	0,36	0,13	0,04	0	**1,35**	0,91
	Mg	4,30	5,72	4,35	4,35	4,08	5,65	**3,08**	3,46
	S	0,08	0,05	0,09	0,08	0,11	0,07	0.08	0,05
Micro Nutriens (%)	Zn	0,01	0,01	0,01	0,01	0,01	0,01	0,02	0,01
	Fe	11,26	13,43	8,16	9,19	11,71	12,03	12,25	13,60
	Mn	0,01	0,02	0,02	0,01	0,02	0,01	**0.05**	0,02
	Si	59,62	54,45	67,22	62,16	61,15	58,05	57,21	54,73
pH	pH	3,71	3,61	3,78	3,65	3,71	3,68	5,58	5,50

Note: T1 (Top Area 1, 0-20cm); S1 (Sub area 1, 20-40cm), T2 (Top Area 2, 0-20cm); S2 (Sub area21, 20-40cm), T3 (Top Area 3, 0-20cm); S3 (Sub area 3, 20-40cm), T4 (Top Area 4, 0-20cm); S2 (Sub area 4, 20-40cm),

Table 1 shows that an increase in pH value is marked by a decrease in Mg content and an increase in Al content. In the topsoil region (0-20cm), an increase in pH is accompanied by an increase in Fe and Mn (Gryboys, M, et al., 2009; Bahera and Shukla., 2014). Generally, changes in pH, when correlated with metal elements, can be signified by changes in elements such as Mg, Al, Fe, Cl, Ca, Zn, Zr, and Mn. The correlation can be seen in **Figure 3**.

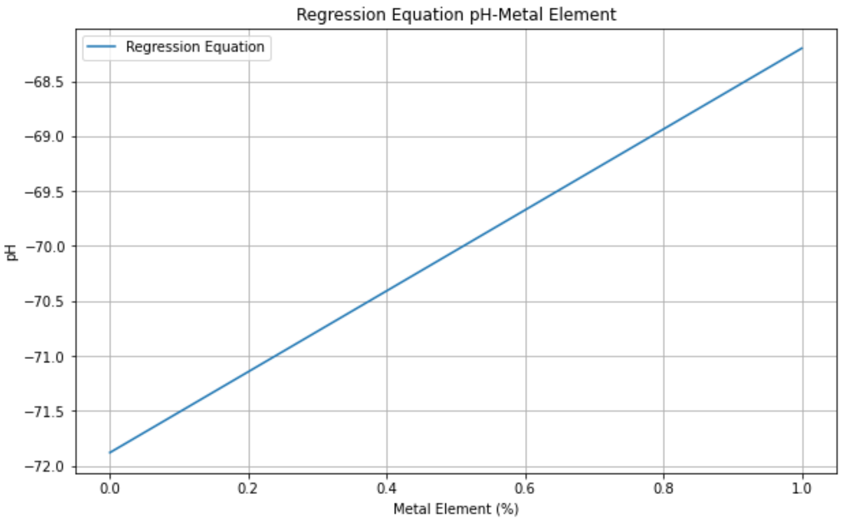

Figure 3. Linear regression of pH against Metal Elements

From **Figure 3**, it can be observed that the correlation between pH value and metal elements is R^2 = 0.938. The distribution of the correlated elements can be seen in **Figure 4**.

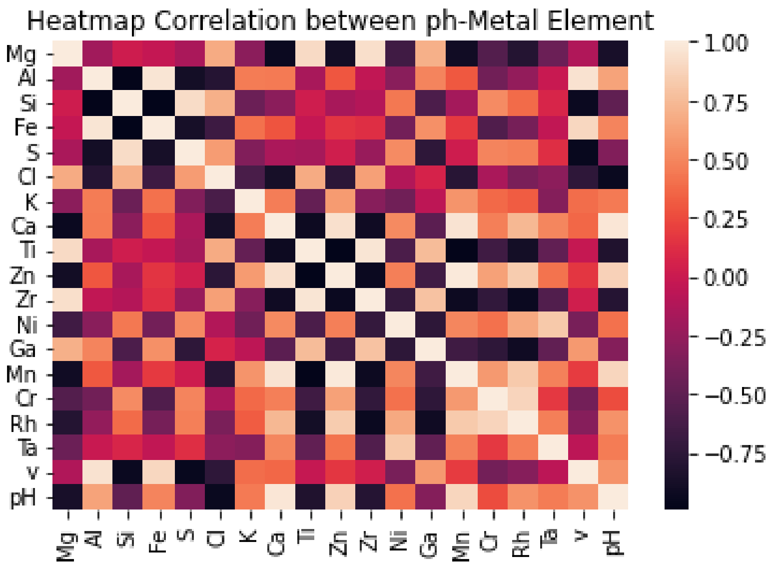

Figure 4. Distribution Map of pH Correlation with Metal Elements

For macronutrients, an increase in pH influences the rise in Ca content and the decrease in Mg content. Therefore, pH changes significantly impact the alteration of macronutrients (Meille, et al., 2021). However, generally, for a pH range of 3.5 – 5.6, there is not a pronounced influence on the changes in macronutrients (N, P, C, and K). The correlation between pH values and macronutrients can be seen in **Figure 5**.

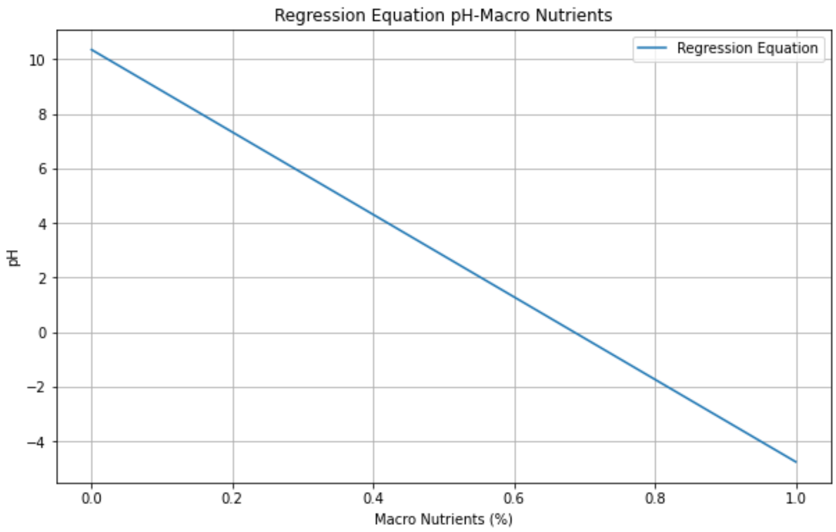

Figure 5. Linear regression of pH against Macro Nutrients

Figure 5 shows strong correlation between pH and macronutriens, with an R2 value of 0.934. The distribution of the correlated elements can be seen in **Figure 6**. For micronutrients, changes occur when there is an increase in pH, leading to an increase in Mn, which is slightly different from some previous research (Bahera and Shukla., 2014). The correlation between pH values and micronutrients can be seen in **Figure 7.**

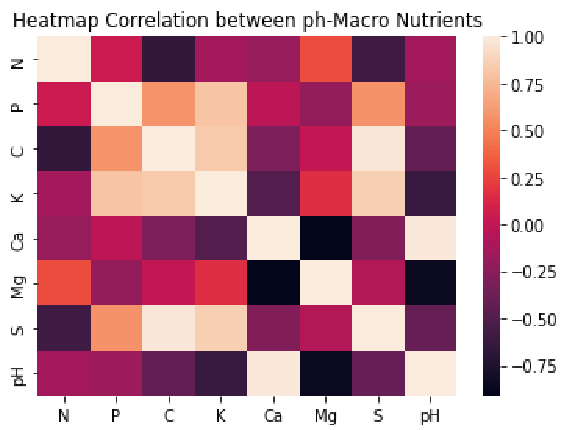

Figure 6. Distribution Map of pH Correlation with Macro Nutrients

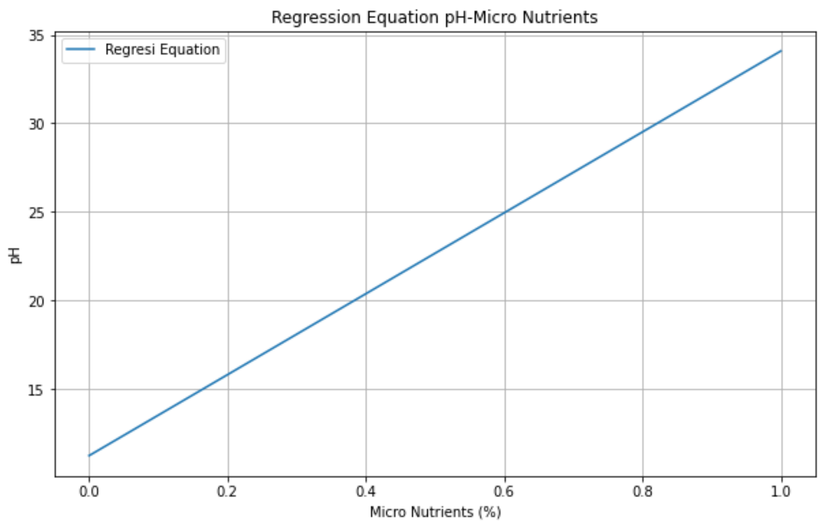

Figure 7. Linear regression of pH against Micro Nutrients

Based on **Figure 7**, it can be observed that the correlation between pH and micro nutrients has an R2 value of 0.767. This correlation is the lowest compared to the correlation of pH with metal elements and macronutrients, but it still represents a relatively strong correlation. The distribution of micronutrients based on the correlation value can be seen in **Figure 8**.

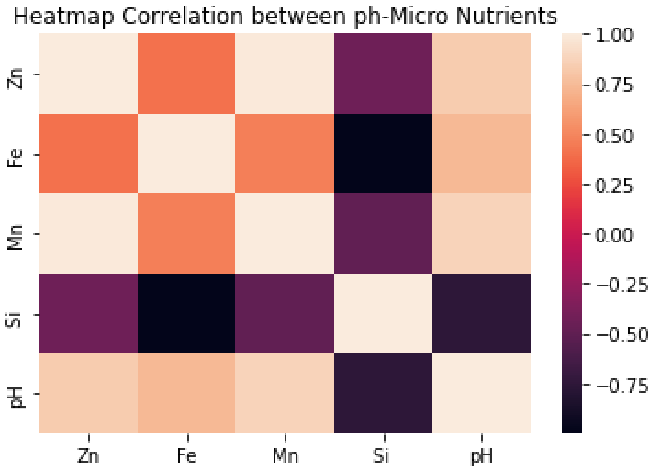

Figure 8. Distribution Map of pH Correlation with Micro Nutrients

CONCLUSION

Metal content, nutrient elements, and pH values have been successfully identified using X-Ray Fluorescence (XRF) and laboratory tests. Subsequent correlation testing of pH values with metal and soil nutrient elements was conducted. The modeling results show that the correlation of pH with metal elements has the highest correlation value compared to its correlation with macro and micronutrients, with an R2 value of 0.938. Then, it is followed by a correlation value with macronutrients of R^2 = 0.934 and micronutrients of 0.767. Based on these correlations, it can be qualitatively concluded that there is a strong relationship between pH values and the presence of metal content, macronutrients, and micronutrients. It can serve as a future estimation model for the soil fertility parameters.

ACKNOWLEDGMENT

We express our gratitude to the Ministry of Education, Culture, Research, and Technology and the Directorate General of Higher Education, Research, and Technology of the Republic of Indonesia for funding this research through the Doctoral Dissertation Education (PDD) 2023 grant scheme.

CONFLICTS OF INTEREST

The authors declare no conflict of interest concerning the publication of this article. The authors also confirm that the data and the article are free of plagiarism.

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