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# Mitigating Heavy Metal Contamination in Agricultural Soils with Biosilica-Humic Acid as Soil Amendment Strategies in Industrial Peripheries

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**Abstract**

Heavy metal contamination in agricultural soils around industrial areas threatens soil fertility, crop productivity, and food safety. This study examined the effectiveness of biosilica–humic acid (BSi-HA) as a soil amendment to reduce the availability of Fe, Mn, Pb, and Cd in paddy soils around pharmaceutical, animal feed, and paper industries in Sidoarjo, East Java. A completely randomized factorial design was used with 15 combinations of industry type and amendment dose (0–40 kg ha$^{-1}$), which were incubated for 60 days. Soil chemical properties and heavy metal availability were analyzed on days 7 and 60 using soil chemical analysis methods and atomic absorption spectrophotometry for metal analysis. The results showed that BSi-HA had no significant short-term effects, but reduced the availability of Fe and Pb after 60 days, with Fe decreasing by 45–67% and Pb by 8–40%. The optimal dose was 10–20 kg ha$^{-1}$, which reduced Fe by 62.52% and Pb by 23.92%. This effect is associated with the –COOH and -OH groups in humic acid, which increase metal adsorption under acidic conditions. Although soil organic carbon and cation exchange capacity decreased during incubation, heavy metal levels decreased in concentration. Overall, BSi-HA shows potential as an environmentally friendly soil amendment to reduce heavy metal contamination and support sustainable land restoration near industrial zones.

## 1. Introduction

The existence of agricultural land is increasingly declining in line with the expansion of industrial areas. The remaining agricultural lands are often located close to industrial zones. Heavy metals commonly found as industrial pollutants of farm soils include Fe, Mn, Pb, and Cd (Shammi et al., 2021). Heavy metals in the soil pose a potential toxic threat to plants. When these metals accumulate in plant tissues, they may also become toxic to humans upon consumption. Previous studies have shown that certain areas in Sidoarjo contain relatively high levels of heavy metals in their agricultural soils. The recorded concentrations were Cu at 54.70 ppm, Zn at 82.28 ppm, Fe at 1171.43 ppm, Mn at 844.25 ppm, Pb at 1.47 ppm, and Cd at 0.37 ppm (Mindari et al., 2023).

Humic substances have three major components: humic, fulvic, and humin. Humic acid is insoluble under low pH conditions, fulvic acid is soluble in low and high pH environments, and humin is insoluble in acidic or alkaline conditions (Sarlaki et al., 2020). Humic acid is an organic compound characterized by dark colors ranging from brown to black. It comprises complex compounds such as aliphatic and aromatic groups (Fatima et al., 2021). Due to its ability to regulate water availability (Herawati et al., 2024), buffer soil pH, and influence redox potential, humic acid is considered suitable as a soil amendment (Yang & Antonietti, 2020). Moreover, its capacity to chelate heavy metals forms the basis for using humic acid in remediating contaminated soils. Studies have found that humic acid can associate with metals such as gold (Au), creating bonds through -COOH and -OH groups (Sarlaki et al., 2020).

Silica is an essential nutrient required by plants and is abundantly found in nature, comprising about 30% of the earth's crust, particularly in rocks and minerals. Silica contributes to plant resistance against both biotic and abiotic stresses. Regarding biotic stress, silica plays a role in defending plants against diseases (Liang & Zhang, 2020). It also enhances crop productivity. A study on rice plants showed that grain weight increased with the addition of silica compared to untreated plants (Siam et al., 2019).

The combination of bio-silica and humic acid has been proven effective in improving soil fertility. Adding bio-silica and humic acid has shown increased nutrient availability in soils with sandy textures. A combination of 1.0 ton ha⁻¹ of bio-silica and 40.0 kg ha⁻¹ of humic acid resulted in $NH_4^+$ and $NO_3^-$ availability of 263.55 ppm, which was higher than other treatments (Mindari et al., 2021). This combination improved soil pH, organic-C content, and CEC. Additionally, it effectively reduced the availability of heavy metals in the soil. Research showed that combining bio-silica and humic acid reduced Pb content by 86.89–90.49% and Cd content by 71.47–76.33% (Chakim et al., 2022).

This study aims to determine the effectiveness of combining biosilica and humic acid in reducing heavy metal availability. Preliminary research has been conducted without combining amendments. In addition, the study also aims to determine the impact of applying amendments to increase the availability of nutrients, organic C, and CEC.

## 2. Material and Method

### 2.1. Research Time and Location

The research was conducted at the Soil Resources Laboratory, Faculty of Agriculture, from October 2023 to May 2024. Soil samples were obtained from agricultural land located near industrial zones in three villages: Industrial Site 1 in Ponakawan Village (7°23'41.9" S, 112°35'37.6" E), Industrial Site 2 in Balong Village (7°23'50.8" S, 112°37'32.5" E), and Industrial Site 3 in Kanigoro Village (7°26'00.8" S, 112°28'28.1" E), all located in Sidoarjo Regency, East Java.

### 2.2. Research Design

The study used an incubation method with soil samples placed in a closed chamber. The experimental design used was a factorial Completely Randomized Design (CRD) with two factors: the type of industry (L) and the dosage of soil amendments (P). The first factor, industry type (L), consisted of three levels: pharmaceutical industry (L1), animal feed industry (L2), and paper industry (L3). The second factor was the dosage of soil amendments: 0 kg ha⁻¹ (P1), 10 kg ha⁻¹ (P2), 20 kg ha⁻¹ (P3), 30 kg ha⁻¹ (P4), and 40 kg ha⁻¹ (P5). These two factors resulted in 15 treatment combinations, each replicated three times, totaling 45 incubated soil samples.

### 2.3. Soil Sampling and Preparation

The soil used in the incubation experiment was carefully sourced from agricultural land close to industrial zones, an area of particular interest due to its potential exposure to industrial pollutants. To ensure consistency and relevance to surface soil processes, samples were manually collected from the upper 0–30 cm layer using a hoe, allowing minimal disturbance to the natural soil profile. This range was selected because it represents the zone most affected by agricultural activities and environmental contaminants. After collecting, the soil samples were air-dried at room temperature in a shaded, well-ventilated area. This step was essential to reduce soil moisture content to a stable level, thereby preventing microbial decomposition and facilitating homogenization before incubation. The air-dried soil was then sieved and stored under appropriate conditions until further use in the experimental treatments.

### 2.4. Soil Amendment (Biosilica-Humic Acid)

The soil amendment was produced by extracting rice husk ash using a strong alkaline solution (10% KOH) at 85°C for 90 minutes, followed by adding a strong acid (1N HCl) to precipitate biosilica at pH 7.0. The biosilica was then purified by washing with distilled water until the chloride (Cl) content was reduced, testing was conducted using the $AgNO_3$ titrimetric method. Subsequently, the biosilica extract was redissolved in 1% KOH to adjust the pH to 9.0, forming a biosilica solution. Humic acid was extracted from compost using a 0.5% KOH solution for 24 hours, followed by the addition of 6N $H_2SO_4$ to adjust the pH to 2, forming a humic acid gel. Approximately 50 g of the humic acid gel was mixed with the pH 9 biosilica solution to create a Biosilica–Humic Acid (Bsi-HA) compound at pH 4.0–5.0. This pH range was chosen to facilitate the chelation of heavy metals. The biosilica solution was added gradually while being stirred using a magnetic stirrer.

### 2.5. Soil Amendment Application and Incubation

The air-dried soil samples were crushed and sieved to obtain particles smaller than 2 mm for homogeneity. A 250-gram portion of each homogenized soil sample (based on oven-dried weight) was placed in a sealed plastic container. The soil amendment was applied by mixing the appropriate dosage (0–40 kg ha⁻¹) with water equivalent to the soil's field capacity. Field capacity was calculated using the following formula.

$$\text{soil water content (\%)} = \frac{(M1-M2)}{M2} x\ 100\% - \%\ dry\ soil\ moisture\ content$$

$$\text{water needed (mL)} = \text{water content (\%) x soil mass (g)}$$

Notes :
M1 = mass of soil to which water has been added
M2 = air-dry soil mass
100% = convert value to %

2.6. Soil Chemistry Analysis

The soil chemical properties were analyzed in three stages: baseline (pre-incubation), seven days after incubation, and 60 days after incubation. The observed parameters included pH, organic-C, total N, available P, and CEC, which were analyzed using a Spectroquant Prove-300 spectrophotometer. The concentrations of Fe, Mn, Pb, and Cd were measured using a Hitachi ZA-3000 Atomic Absorption Spectrophotometer (AAS). The procedures followed the 2023 Technical Guidelines for the Chemical Analysis of Soil, Plant, Water, and Fertilizer issued by the Soil and Fertilizer Instrument Standards Testing Center (BPSI Tanah dan Pupuk, 2023).

2.7. Data Analysis

The data obtained from the experiment were analyzed using Analysis of Variance (ANOVA) at a 5% significance level. If significant differences among treatments were detected, a post hoc analysis using the Tukey's Honestly Significant Difference (HSD) test at the 5% level was performed. Additionally, a paired t-test was used to determine differences before and after applying the soil amendment. Correlation and regression analyses were also conducted for each observed variable with Microsoft Excell v.16.

## 3. Result and Discussion

3.1. Initial Soil Analysis

The rice field area selected as the soil incubation medium was located near several industrial zones, including pharmaceutical, animal feed, and paper manufacturing facilities. These industries were chosen due to their varying pollution potentials, which stem from the nature of their raw materials, the complexity of their production processes, and the types of chemical waste they generate. For instance, pharmaceutical industries may discharge organic compounds and trace metal residues. At the same time, animal feed factories can contribute nutrient overloads and biologically active substances, and paper mills often release effluents rich in heavy metals, chlorine compounds, and other industrial (Mohammadi et al., 2020). These emissions, whether through air, water, or soil pathways, can accumulate in nearby agricultural fields and lead to elevated concentrations of potentially toxic elements, heavy metals such as Cd, Pb, Mn, and Fe. The presence of these contaminants in the soil poses serious risks to crop health, food safety, and overall soil fertility. Continuous exposure to such pollutants may impair plant growth (Dewi et al., 2023), reduce yields, and accumulate hazardous substances in edible plant parts, affecting human and animal health through the food chain (Cai et al., 2024).

The chemical properties of several fields (Table 1) show relatively uniform values, particularly in terms of pH, organic C, total N, and CEC of the soil. The pH values from the three sites indicate neutral criteria (BPSI Tanah dan Pupuk, 2023). These values fall within the suitable range for rice plant growth and cultivation between 5.5 and 7.3 (Dengiz et al., 2010). The organic C content in the soils from the three locations ranges from 1.86% to 2.91%, which was classified as low to moderate (BPSI Tanah dan Pupuk, 2023). This level of organic C is considered adequate for use as rice cultivation land (Muttaqien et al., 2020).

Table 1. Chemical and physical properties of the initial soil for incubation media

| Code | pH $H_2O$ | Org-C | Tot-N | Avail-P | CEC | Sand | Silt | Clay | Texture Class |
|---|---|---|---|---|---|---|---|---|---|
| | - | % | % | ppm | cmol/kg | % | % | % | |
| Industry 1 | 7.04 | 2.20 | 0.18 | 27.21 | 44.34 | 7 | 67 | 26 | Silty Clay |
| Industry 2 | 6.97 | 2.91 | 0.21 | 34.73 | 38.88 | 3 | 74 | 23 | Silty Clay |
| Industry 3 | 6.97 | 1.86 | 0.11 | 18.02 | 33.80 | 29 | 49 | 22 | Clay |

Notes: Land Resources laboratory test results 2024; Org=organic; tot=total; avail=available; CEC=cation exchange capacity

The soil's total N content categorized into low, ranging from 0.11-0.21%, thus required if the land is used for crop cultivation. The available phosphorus (P) is categorized as very high (>20 ppm), and the soil's CEC falls into the high to very high category (>40 cmol $kg^{-1}$) (BPSI Tanah dan Pupuk, 2023). Although the total nitrogen content is only moderately suitable, the high phosphorus level is appropriate for rice cultivation (Kong et al., 2022). The cation exchange capacity (CEC) is also considered suitable for rice crops (Mindari et al., 2023). The CEC values of the three land sites vary due to differences in the soil texture classes. Industrial locations 1 and 2 do not differ significantly because their clay, silt, and sand fractions are relatively similar. However, location 3 has a sand content of 29%, which is higher than that of the other sites. Soils with a high sand fraction are more susceptible to fertility decline because of their lower nutrient retention capacity (Tiemann & Douxchamps, 2023). This condition is evident in location 3, where overall NPK nutrient levels in the soil are lower compared to the other two sites. The higher sand fraction at location 3 is likely the cause of the lower CEC value observed at that site (Sukarman & Gani, 2020).

Table 2. Heavy metal content available in the nearest rice field soil at the industrial location (initial)

| **Code** | **Avail-Fe** | **Avail-Mn** | **Avail-Pb** | **Avail-Cd** |
|---|---|---|---|---|
| | **mg kg$^{-1}$** | | **µg kg$^{-1}$** | |
| Industry 1 | 486.22 | 122.43 | 495.10 | 77.62 |
| Industry 2 | 537.23 | 158.79 | 558.04 | 69.23 |
| Industry 3 | 507.61 | 90.71 | 411.19 | 31.47 |

Notes: Laboratory test results for Land Resources at UPN Veteran East Java; avail=available

Each site's available heavy metal content (Table 2) is categorized below the safety threshold. Fe levels range from 486.22 to 537.23 mg kg$^{-1}$ (<38,000 mg kg$^{-1}$), Mn from 90.71 to 158.79 mg kg$^{-1}$ (<850 mg kg$^{-1}$), Pb from 411.19 to 558.04 µg kg$^{-1}$ (<0.5 mg kg$^{-1}$), and Cd from 31.47 to 77.62 µg kg$^{-1}$ (3–8 mg kg$^{-1}$) (Khasanah et al., 2021). Heavy metals in the soil contribute to a decline in the soil quality index. Previous studies have shown low to moderate soil fertility index values, with pharmaceutical industry sites scoring 0.44–0.63, animal feed industry sites 0.42–0.52, and paper industry sites 0.44–0.55 (Mindari et al., 2023). Biosilica binds heavy metals through adsorption, a mechanism whereby heavy metals such as Pb bind to the –OH groups present in the Si-OH group (Lei et al., 2018). An application dosage of 40 mg kg-1 with a pH of 7 increased the –COOH and –OH content and formed a complex with Fe metal (Boguta et al., 2019).

3.2. Characteristics of Biosilica-Humic Acid with SEM-EDX

Biosilica combined with humic acid forms a new soil amendment material known as biosilica-humic acid (Bsi-HA). This soil amendment, which is reacted under pH 5.0 conditions, aims to bind heavy metals available in the soil solution. Research has shown that pH levels of 5.0–6.0 can enhance the binding of Pb at pH 5.0 and Cd at pH 6.0 (Chakim et al., 2022). Humic acid is obtained through the extraction of organic matter using a strong alkaline solution and is formed into solid humic acid at pH 2.0 using a strong acid (Mindari et al., 2022). Biosilica is derived from the extraction of rice husk ash with an alkaline solvent and forms a gel upon the addition of acid until reaching pH 7.0 (Luthfiah et al., 2021). The soil amendment was produced by extracting rice husk ash using a strong alkaline solution (10% KOH) at 85°C for 90 minutes, followed by adding a strong acid (1N HCl) to precipitate biosilica at pH 7.0

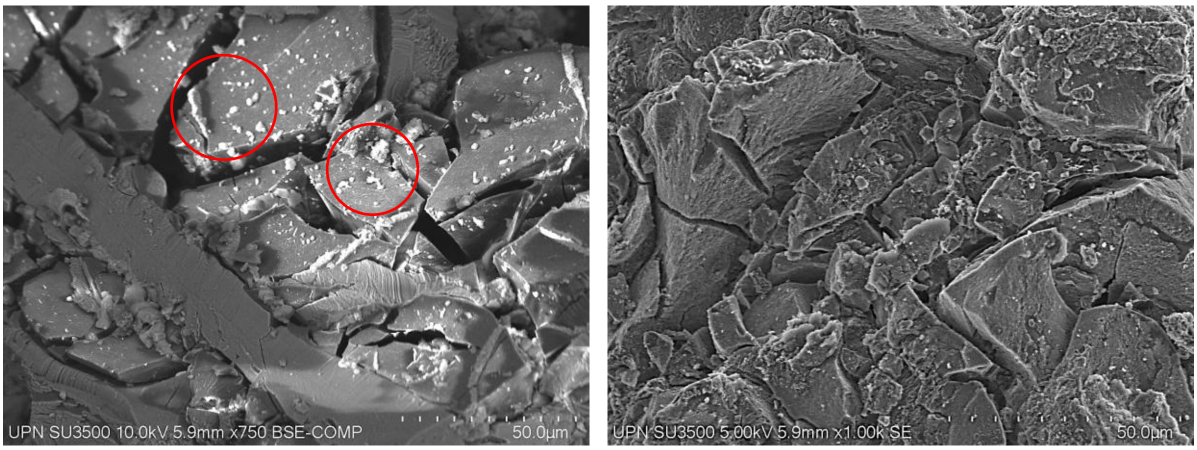


Figure 1. (A) Results of surface analysis of Biosilica-Humic acid with magnification x750 and (B) Biosilica-Humic acid with magnification x1000

Surface analysis using the Scanning Electron Microscope (SEM) method was conducted to observe the surface morphology of the biosilica and humic acid mixture. SEM observations (Figure 2A) at 750x magnification revealed silica as granules attached to the humic acid structure. Silica obtained from acid precipitation, whether using $H_2SO_4$ or HCl, tends to form an amorphous (irregular) structure (Hindarso et al., 2021). The humic acid structure at 1000x magnification shows surface cracks. At pH 5.0, humic acid forms aggregated structures that appear as irregularly shaped spheres (*irregular shape*) (Sarlaki et al., 2020).

Table 3. SEM-EDX test results with the BSi-AH sample

| Elements | Weight (%) | Atom (%) |
|---|---|---|
| Carbon (C) | 19.10 | 29.14 |
| Nitrogen (N) | 4.52 | 5.92 |
| Oxygen (O) | 40.79 | 46.73 |
| Silica (Si) | 3.34 | 2.18 |
| Phosphorus (P) | 0.45 | 0.27 |
| Sulfur (S) | 5.41 | 3.09 |
| Clor (Cl) | 6.26 | 3.24 |
| Kalium (K) | 20.12 | 9.43 |

Notes: Results of SEM-EDX at the LPT Instrumentation Laboratory of UPN Veteran East Java

Characterization of BSi-HA was carried out using the SEM-EDX method. The purpose of using this method is to analyze the surface morphology and determine the elemental composition. SEM-EDX analysis showed that the elemental composition of BSi-HA (Table 3) includes silicon (Si) at 3.34%, carbon (C) at 19.10%, and oxygen (O) at 40.79%. Total-K content at 20.12% in BSi-HA originates from the biosilica and humic acid solvent, which uses potassium hydroxide (KOH). The most abundant element in BSi-HA is oxygen (Figure 3), with a weight percentage of 40.79%, due to functional groups in biosilica such as Si–O–Si (Schaller et al., 2020). Humic acid contains functional groups such as –COOH, –OH, phenol, and –C=O (Chakim et al., 2022).

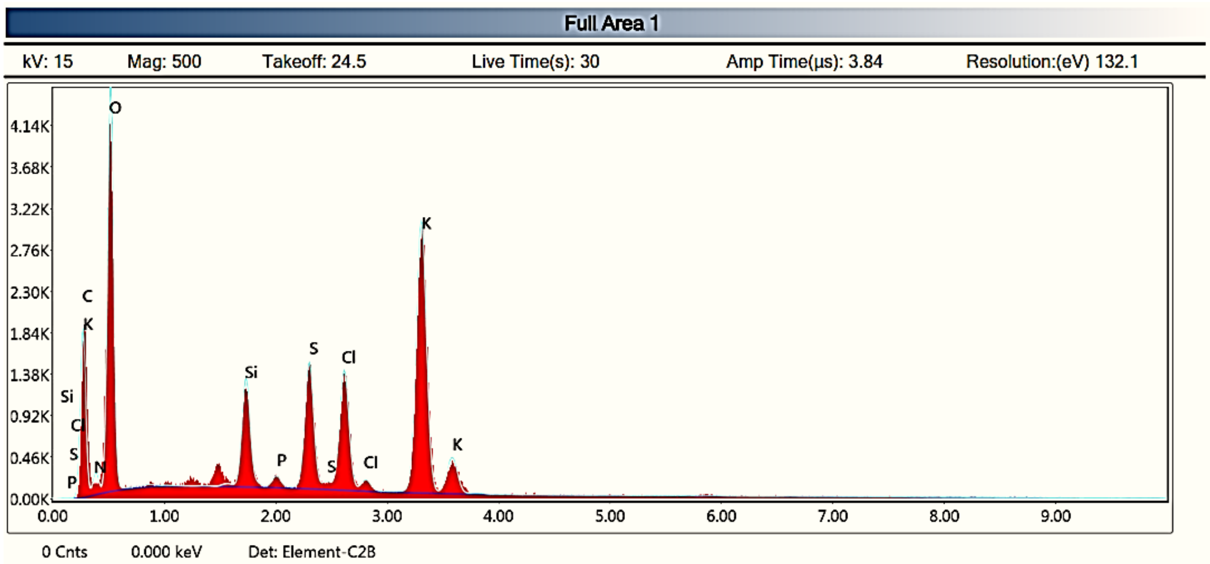


Figure 2. Graph of SEM-EDX chemical element analysis results in Biosilica-Humic Acid (BSi-AH)

### 3.3. The Effect of Biosilica-Humic Acid (BSi-AH) on Soil Chemical Properties

This study's observation of soil chemical properties included pH ($H_2O$), organic C, total N, available P, and CEC. Observations were conducted at two time points: 7 and 60 days after the soil was incubated with the biosilica-humic acid (BSi-HA) soil amendment. The BSi-HA treatment was applied at the beginning when the soil medium was prepared, with amendment doses of 0, 10, 20, 30, and 40 kg $ha^{-1}$. The results showed that the first observation (Table 4) did not reveal any significant changes caused by the soil amendment. Statistical analysis using analysis of variance (ANOVA) indicated that the soil amendment factor did not significantly affect any of the tested parameters. On the other hand, differences in land location were found has a significant influence the tested parameters, as shown by the ANOVA test at the $p<0.05$ significance level.

Table 4. Condition of soil chemical properties after 7 and 60 days of incubation with soil conditioner

| Treatment Code | pH $H_2O$ | | Org-C (%) | | Tot-N (%) | | Avail-P (ppm) | | CEC (cmol (+) $kg^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 7 dai | 60 dai | 7 dai | 60 dai | 7 dai | 60 dai | 7 dai | 60 dai | 7 dai | 60 dai |
| P0 (0 kg $ha^{-1}$) | 6.69 | 6.66 | 1.97 | 1.93 | 0.15 | 0.15 | 28.91 | 28.83 | 50.15 | 38.67 |
| P1 (10 kg $ha^{-1}$) | 6.74 | 6.76 | 2.02 | 1.92 | 0.14 | 0.15 | 29.46 | 29.47 | 50.23 | 36.40 |
| P2 (20 kg $ha^{-1}$) | 6.75 | 6.76 | 2.05 | 1.90 | 0.14 | 0.15 | 29.62 | 29.35 | 46.75 | 36.35 |
| P3 (30 kg $ha^{-1}$) | 6.74 | 6.74 | 2.02 | 1.90 | 0.15 | 0.16 | 31.13 | 31.61 | 44.39 | 36.85 |
| P4 (40 kg $ha^{-1}$) | 6.79 | 6.74 | 2.11 | 1.78 | 0.16 | 0.16 | 33.00 | 31.75 | 49.42 | 39.19 |
| *Tukey's HSD $p<0.05$* | **0.60** | **0.14** | **0.58** | **0.03** | **0.47** | **0.04** | **0.22** | **0.58** | **0.25** | **0.13** |
| L1 (Industry 1) | 6.78ab | 6.77b | 2.25b | 2.08b | 0.15b | 0.15a | 31.85b | 32.20ab | 49.21a | 40.01b |
| L2 (Industry 2) | 6.54a | 6.51a | 2.33b | 2.13b | 0.18b | 0.20a | 36.61b | 37.13b | 53.06a | 43.69b |
| L3 (Industry 3) | 6.92b | 6.93b | 1.51a | 1.45a | 0.10a | 0.11a | 22.81a | 21.28a | 42.29a | 28.77a |
| *Tukey's HSD $p<0.05$* | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** |

Notes: Numbers in the same column and followed by the same letter notation indicate results that are not significantly different in the Tukey's HSD follow-up test, $p<0.05$; dai=days after incubation; avail=available; tot=total; org=organic; CEC=cation exchange capacity

The chemical properties of the soil observed at the final time point, 60 days after incubation, showed changes in several parameters. A decrease in the soil's CEC was observed 60 days after incubation, corresponding with a decline in soil organic C content. A t-test analysis (Table 5) showed significant changes in organic carbon values between 7 and 60 days after incubation; the CEC values also showed significant differences. The decline in soil organic carbon may be attributed to microbial activity during incubation (Dewi et al., 2022), in which microbes decompose carbon and release $CO_2$ as part of their metabolic processes (Ren et al., 2022) since soil CEC is partly influenced by the presence of organic C, a reduction in organic C levels will affect the soil's CEC. The nitrification process by microbes produces $H^+$ ions that lower soil pH, thereby reducing the number of deprotonated carboxyl and phenolic groups and decreasing the negative charge of colloids (Wang et al., 2020). In addition, the rapid decomposition of organic matter by microbes causes the loss of the main source of organic charge, thereby reducing the contribution of organic matter to CEC. Microbes also produce organic acids such as citrate and oxalate that can dissolve $Al^{3+}$ and $Fe^{3+}$, where these positively charged cations neutralize the negative charge of the soil and reduce the effective CEC. Furthermore, the mineralization of organic matter increases the mobility of easily leached base cations ($Ca^{2+}$, $Mg^{2+}$, $K^+$), thereby decreasing base saturation and reducing soil (Pachideh et al., 2021).

Table 5. Results of the t-test of soil chemical properties between 7 and 60 days of soil conditioner incubation

| | pH $H_2O$ | Org-C | Tot-N | Avail-P | CEC |
|---|---|---|---|---|---|
| ***t-Test $p<0.05$*** | 0.48 | **0.00*** | 0.16 | 0.72 | **0.00*** |

Notes : * = significantly results in the t-test $p<0.05$

3.4. Availability of Heavy Metals in Soil

The presence of heavy metals in soil poses a potential threat to the sustainability of crop cultivation. Heavy metals in soil are classified into two types: essential and non-essential. Essential metals, such as copper (Cu), zinc (Zn), and nickel (Ni), are needed by plants for metabolic activities (Bibi et al., 2023). In contrast, non-essential metals like lead (Pb) and cadmium (Cd) are considered contaminants that pose risks to plants. However, even essential metals can become contaminants if their concentrations exceed threshold limits in the soil. The safety thresholds are Fe > 38,000 mg $kg^{-1}$, Mn > 850 mg $kg^{-1}$, Pb 100–200 mg $kg^{-1}$, and Cd 3–8 mg $kg^{-1}$ (BPSI Tanah dan Pupuk, 2023).

Observations of heavy metal content at 7 and 60 days after incubation showed no significant differences (Table 6) due to the soil amendment factor. However, significant differences were observed based on the industrial site factor, with Fe, Mn, Pb, and Cd levels varying significantly between locations. Overall, the heavy metal levels at all sites remained below the safe contamination thresholds, though they still present potential risks in the future if not managed properly.

The overall impact of applying the BSi-HA soil amendment did not show significant results. However, statistical t-test analysis between 7 and 60 days after incubation indicated a significant decrease (Table 7) in Fe and Pb concentrations. The reduction in Fe levels between 7 and 60 days after incubation with the addition of BSi-HA ranged from 45–67%, while Pb levels decreased by 8–40%. The effectiveness of the BSi-HA combination is supported by the functional groups in both silica and humic acid. The –COOH and –OH functional groups in humic acid have strong adsorption capacities at pH 5 (Boguta et al., 2019). The –OH functional group content in biosilica is much lower than in humic acid. Carboxyl groups (–COOH) enhance the soil amendment's ability to bind heavy metals (Chakim et al., 2022). The combination of biosilica and humic acid has been proven to reduce the availability of heavy metals. The content of Pb and Cd in plant tissues can be reduced by as much as 86–90% for Pb and 71–76% for Cd (Chakim et al., 2022).

Table 6. Availability of heavy metals 7 and 60 days after incubation (hsi) with soil conditioners

| **Treatment Code** | **Avail-Fe (mg kg$^{-1}$)** | | **Avail-Mn (mg kg$^{-1}$)** | | **Avail-Pb (µg kg$^{-1}$)** | | **Avail-Cd (µg kg$^{-1}$)** | |
|---|---|---|---|---|---|---|---|---|
| | **7 dai** | **60 dai** | **7 dai** | **60 dai** | **7 dai** | **60 dai** | **7 dai** | **60 dai** |
| P0 (0 kg ha-1) | 413.00 | 155.06 | 77.97 | 82.93 | 573.43 | 467.13 | 58.74 | 42.73 |
| P1 (10 kg ha-1) | 412.72 | 155.06 | 68.81 | 75.39 | 538.46 | 481.12 | 57.34 | 40.63 |
| P2 (20 kg ha-1) | 392.16 | 166.12 | 84.41 | 72.14 | 615.38 | 453.15 | 56.64 | 55.31 |
| P3 (30 kg ha-1) | 423.69 | 179.11 | 80.45 | 73.74 | 531.47 | 481.12 | 54.55 | 57.48 |
| P4 (40 kg ha-1) | 413.27 | 163.08 | 83.71 | 71.30 | 531.47 | 460.14 | 50.35 | 47.69 |
| *HSD Tukey's p<0.05* | **0.53** | **0.40** | **0.85** | **0.29** | **0.68** | **0.83** | **0.35** | **0.43** |
| L1 (Industry 1) | 371.53 | 160.87a | 80.05 | 84.39b | 625.17 | 595.80b | 80.14b | 49.93 |
| L2 (Industry 2) | 451.83 | 157.22a | 75.85 | 97.57b | 583.22 | 444.76ab | 61.68b | 38.27 |
| L3 (Industry 3) | 409.54 | 172.97a | 81.31 | 43.33a | 465.73 | 365.03a | 24.76a | 58.11 |
| *Tukey's HSD p<0.05* | **0.00** | **0.32** | **0.29** | **0.00** | **0.04** | **0.00** | **0.00** | **0.10** |

Notes: Numbers in the same column and followed by the same letter notation indicate results that are not significantly different in the Tukey's HSD follow-up test, p<0.05; dai=days after incubation, avail=available

Table 7. Results of the t-test of heavy metal availability between 7 and 60 days of soil amendment incubation

| | **Avail-Fe** | **Avail-Mn** | **Avail-Pb** | **Avail-Cd** |
|---|---|---|---|---|
| ***t-Test p value <0.05*** | **0.00*** | 0.61 | **0.00*** | 0.45 |

Notes : * = significantly different results in the t-test p<0.05; avail=available

## 3.5. Recommendations for Soil Management and Amendment

Rice fields are the most vulnerable to heavy metal contamination due to their proximity to industrial areas. Several metals, such as Fe, Mn, Pb, and Cd, are commonly found heavy metals. This situation requires special treatment in both industrial and rice field areas. The importance of prevention and mitigation systems to be implemented in handling heavy metal contamination in rice fields, where prevention can take the form of government regulations on industrial area management. Meanwhile, mitigation can take the form of utilizing soil remediation models to reduce the availability of heavy metals in the soil.

Requires the participation of the government, industry, and farmers in industrial areas. Environmental management is necessary to reduce the risks that can be caused by metal pollution (Chen & Ding, 2023). The government's role in regulating industrial and agricultural areas must prioritize balanced interests. Government regulations must emphasize supervision and sanctions for industries that produce pollution. The government, in its role as policy maker and implementer, must establish long-term supervision mechanisms with high pressure and normalization trends that place equal emphasis on company supervision and inspection, comprehensively using policy implementation methods, and strictly punishing corporate non-compliance and governance (Xu et al., 2020).

Mitigation of land exposed to heavy metal contamination aims to reduce the risk of increased pollution. This can be done through soil remediation methods to reduce the amount of heavy metals available. Methods that can be used include phytoremediation, electrokinetic, natural attenuation, soil washing and soil solidification (Adnan et al., 2022). Natural attenuation is a natural method such as advection, dispersion, sorption, and biotic and abiotic reactions without active intervention. The use of this method is relatively easy to implement by local farmers using several natural materials found around the farm. One of the materials that can be used is BSi-HA, which is obtained from natural compost and rice husk ash (Chakim et al., 2022). Research shows a decrease in the bioavailability of heavy metals Fe and Pb where the recommended dose is 10-20 kg ha$^{-1}$. The results show a 62.52% decrease in Fe and a 23.92% decrease in Pb, proving that the application of BSi-HA can reduce the availability of heavy metal contamination. These results are consistent with previous studies that the combination of silica and humic acid can suppress heavy metal concentrations through the adsorption system (Chakim et al., 2022).

## 4. Conclusion

The application of biosilica-humic acid (BSi-HA) as a soil amendment did not show any immediate effects within 7 days of incubation. However, significant changes were observed after 60 days, particularly a decrease in heavy metal availability. Iron (Fe) levels decreased by 45–67% and lead (Pb) by 8–40%, demonstrating the potential of BSi-HA in binding metals. This effect is supported by functional groups, particularly –COOH and –OH, in humic acid, which are effective in metal adsorption under acidic conditions. Although soil organic carbon content and cation exchange capacity (CEC) decreased during incubation, heavy metal concentrations remained below critical thresholds, but there was a noticeable reduction in heavy metals. The optimal dose of 10-20 kg $ha^{-1}$ showed a 62.52% reduction in Fe and a 23.92% reduction in Pb. These findings indicate that BSi-HA can improve soil quality in contaminated areas by reducing metal availability. Therefore, it can be recommended that the application of BSi-HA provides an alternative for the remediation of heavy metal-contaminated soil. Further research is recommended to evaluate its long-term effects on plant safety and productivity. Overall, BSi-HA offers a promising environmentally friendly strategy for soil remediation near industrial zones.

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